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VOLUME XV SEPTEMBER 6, 1926 NUMBER 15

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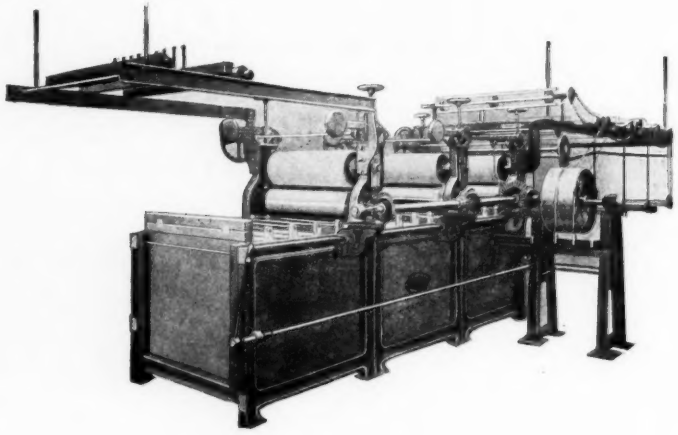

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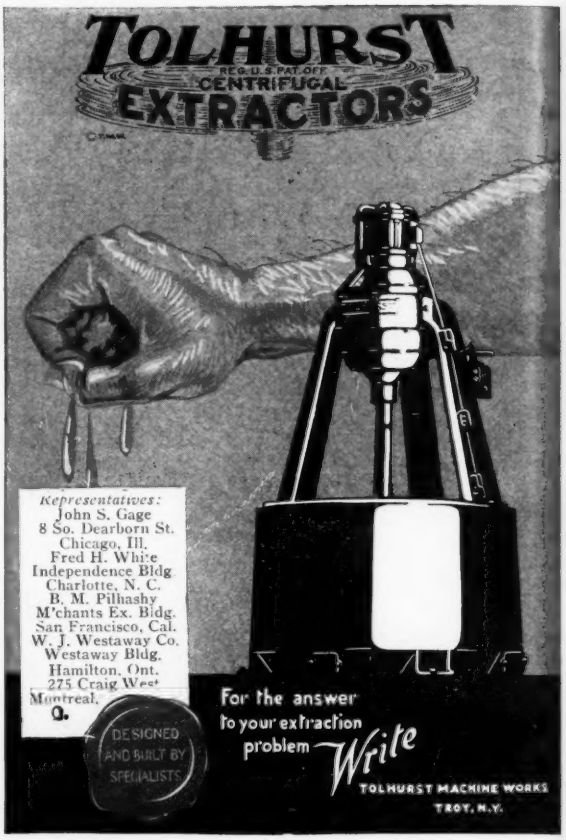

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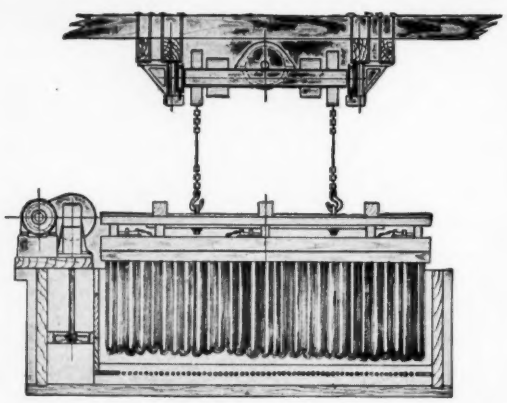

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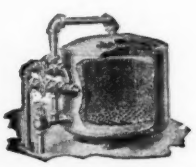

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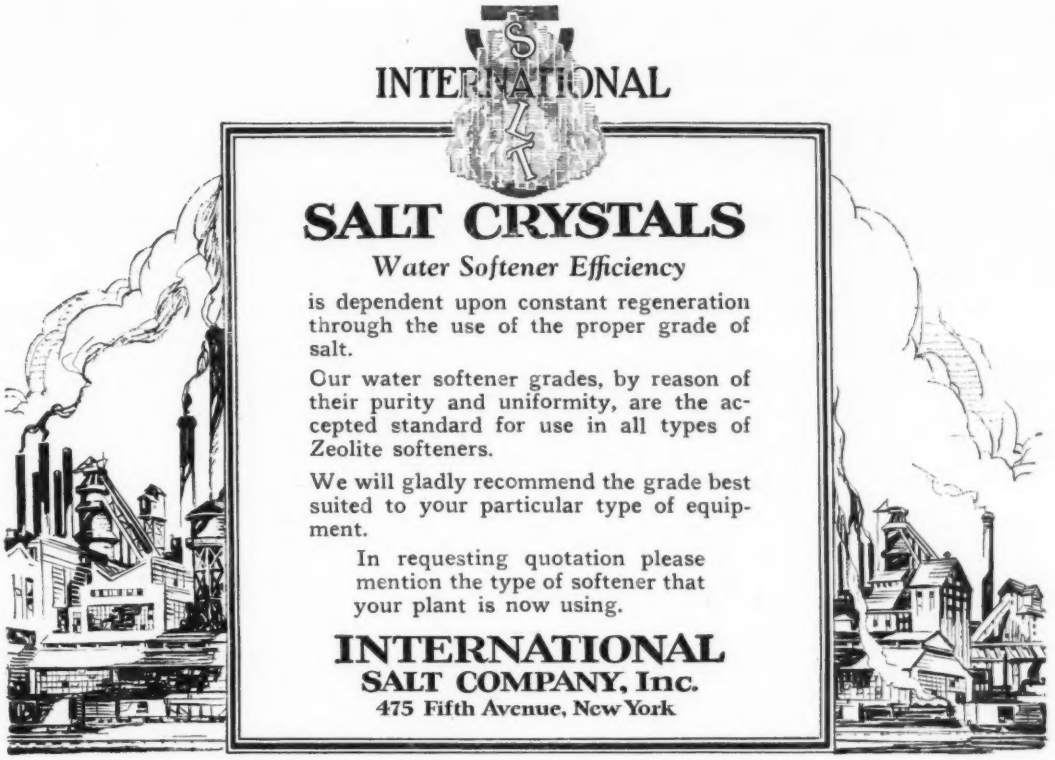

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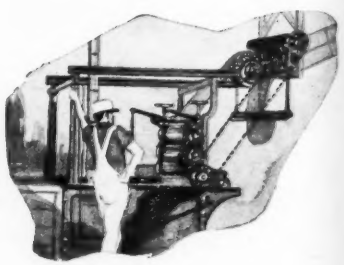

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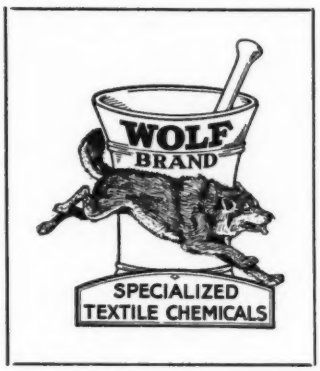

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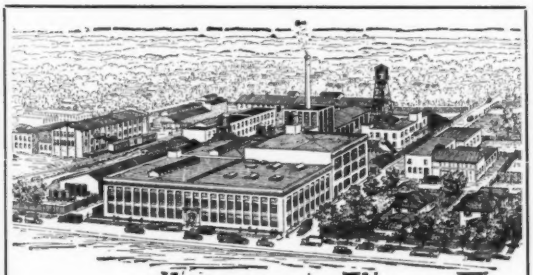

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VOLUME XV NEW YORK, SEPTEMBER 6, 1926 No. 15

Aniline Poisoning from the Dye Bath?

Exaggeration of Aniline Poisoning—Poison in Dye Manufacture—Possibilities of Poisoning During Dyeing —Poisoning in Aniline Black Dyeing—Absorption of Dye from the Bath

By FREDERICK S. BEATTIE

Assistant Professor of Organic Chemistry, Lowell Textile School

WE are more or less humorously accustomed to the loose phraseology and distorted facts of what is termed "newspaper science," and to the use, in the daily papers, of the magic word "aniline," both as referring to occasional mysterious cases of poisoning, and to the classification of all synthetic dyes as "analine dyes." It is a matter of graver concern, however, that so many supposedly well-informed physicians so readily condemn the modern valuable synthetic organic medicinal agents, as aspirin, antipyrin, etc., on the ground that they are "Aniline" or "Coal-tar" products. And aniline is thus blamed, when, perhaps, even probably, some other simple organic compound is involved. Modern medicine gratefully acknowledges its debt to more than a few synthetic substances of organic nature; in fact, most of the genuine triumphs of modern medicine are owing to these artificial drugs, which are too often glibly condemned by the ill-informed as "aniline derivatives," as though that phrase ruled them out of court at once.

Perhaps almost any chemical, organic or inorganic, may be considered as poisonous, beyond certain limits. Common salt, for example, if taken into the stomach in amounts beyond dietary requirements, usually acts as a rather prompt emetic. And aniline certainly ought not to be used as a scapegoat, upon whose head almost any case of poisoning from an organic source may be safely laid.

It would seem that somewhat recently there has appeared in some publication an article in which reference has been made to cases of "aniline poisoning," affecting certain silk dyers, the aniline being liberated from the dye bath in the process of dyeing. We have not seen the article in question, but within the past three months two separate inquiries have been directed to the editor of this journal, from two bureaus of public health, in two widely separated universities, asking for information as to whether such cases of aniline poisoning are really possible. The inquiry is of some importance. If the poisoning of a dyer, silk or otherwise, by vapors from the boiling dye bath, is at all possible, the subject is one requiring immediate attention from the health authorities of any place where dyeing is carried on. It has seemed advisable, therefore, to look carefully into the question—it is possible for aniline vapor, or, to make the inquiry very broad, the vapor of any organic compound, or inorganic compound, to be evolved from the dye bath?

Poisons in Dye Manufacture

It is, of course, well known that in the manufacture of dyes many very poisonous, even highly dangerous, chemicals are necessarily employed, most of which do or can set free vapors, or which are used in a particular process as vapor or gas. Nitrous fumes in nitration and diazotization, sulphur trioxide vapors in sulphonation, carbon disulphide, hydrochloric acid gas, carbon monoxide, hydrocyanic acid, all these common and dangerous inorganic substances, as gas or vapor, are commonplace incidents in the chemical plants. Nitrobenzene, aniline, phenol or carbolic acid, and all their simple and complex homologues and derivatives, are unavoidable incidents in the synthesis of even simple dyes, for it is from these and the like substances that dyes as well as pharmaceuticals are built up.

To cite a specific example, that of the very simple

dye, Orange II; in the synthesis of this dye the workman is exposed successively to the dangerous influence of benzene vapor, nitrous fumes, aniline vapor, nitrous fumes again, fused and spattering caustic soda, and sulphur dioxide. Yet a workman, in producing this very simple dye, is not endangered, for the vapors, etc., are all taken care of by proper ventilation; and grave carelessness alone will make it possible for the workman to be even inconvenienced by any of the vapors or gases mentioned. Thus, even in the most dangerous stage of the life of a dye, if it may be so expressed, where all the dangerous volatile material is directly involved in the free state, there are very few cases indeed in which poisoning can take place, unless the workman deliberately thrusts himself into the poisonous atmosphere.

Possibilities of Poisoning During Dyeing

But the question under consideration is of the possibility of poisoning (specifically by aniline, but here considered much more broadly) from the evolution of vapors from the dye bath, in the application of the dye to a fabric or fiber.

If such an occurrence is possible, the substance (aniline, let us say) must either be present as such in the dye as sent out from the factory and employed in solution in the dyehouse, or else it must be split off or regenerated from the dye in the boiling dye bath. These are the only two possibilities. The first may be pronounced impossible nowadays, for the presence of any free oily matter, such as aniline, in a dye, would render the dye more or less sticky, pasty powder, impossible to weigh carefully in making up the bath. Dyers are particular about the physical properties of the dyes which they use, and object to using a dye which is not a good, clean, dry-looking powder. Further, no manufacturer can afford to turn out a product which is contaminated with an oily impurity, for the amount of the contaminating substance would necessarily vary from lot to lot; and uniformity of various shipments of a given dye is one of the most stringent requirements which the dye manufacturer has to meet. The manufacturer who turns out a sticky, variably impure line of dyes does not remain in business for many months.

As to the second possibility, that of aniline or a similar substance being split off from the dye in the dye bath, we may brand it also as an impossibility at once. A dye, under the worst or most severe conditions, is applied in boiling aqueous solution, with the addition, in the bath, of such various practically inactive substances as common salt, Glauber's salt, acetic or formic acid, or very dilute sulphuric acid. Further, these can in no way split off aniline or any similar substance from a dye, in aqueous solution of the highest concentration. Further, if the dyer, in making up his bath, were to make a totally uncalled-for addition to the bath, which could possibly accomplish such a cleavage of the dye-molecule, the dye would in that case simply be destroyed, and the bath made useless for dyeing, with the added result that the powerful reagent used would almost certainly destroy the fiber or fabric as soon as the latter was entered. And further still, all the dyes used commercially are known positively not to decompose, with the liberation of any organic substance, under any condition possible in the dye bath.

Poisoning in Aniline Black Dyeing

There is only one case in which aniline vapors may be encountered. We refer to the dyeing of aniline black. Here, as is known, we are dealing with a dye which, on account of its extreme insolubility, cannot be applied in the ordinary way, nor can it be "vatted," as reduction destroys it. Aniline black must be applied by producing it in the fiber of the fabric, by means of some oxidizing agent acting upon the fabric previously impregnated with a salt of aniline, applied in aqueous solution. But here we are dealing, not with free aniline, but a salt of it; and the salts of aniline do not volatilize with steam, even though a steaming temperature is used. And as the oxidizing agents used are of either neutral or acid nature, it is plain that no free aniline can be liberated in this case also. It is true that in some dyehouses the aniline salt employed (the hydrochloride) is prepared from aniline oil (free aniline) rather than purchased ready prepared, and in that case aniline vapor might conceivably be discharged into the air through improper mixing of acid and base, and consequent overheating. But such a possibility could not be laid to the account of dyes or dyeing; merely to the preparation of a chemical, which might better have been purchased ready prepared.

In aniline black dyeing, the aniline is invariably used as the so-called "aniline salt," the hydrochloride; and in the manufacture of this substance on the large scale the two components, aniline oil and concentrated hydrochloric acid, are simply mixed in the proper proportions, the hot, thick paste solidifying, on cooling, to a moist cake of crystals, in which a small excess of the acid should be present; this crystalline product being centrifuged and then well dried. Such a product is netirely neutral; that is, contains no free aniline or hydrochloric acid, and is perfectly safe to use. When, however, this process is imitated on the small scale in the dyehouse, owing both to lack of facilities for centrifuging and drying, and to the immediate need for the product, the salt is prepared by mixing roughly, and adding more aniline than will combine with the acid bath, for in the mixture and free hydrochloric acid still present would produce destructive tendering of the goods. While such a product is used, the

free aniline will of course be delivered into the atmosphere of the dyehouse on steaming, or even on lying about in the warm air of the works. If, then, poisoning of a workman has taken place from such a source, it must be ascribed to improper preparation of materials.

We have seen only one instance referred to in the literature, in which any substance is definitely split off in the dye bath; namely, that of the nitrosated Tropaeolin or Orange IV, known as Indian Yellow. This dye, which is often used in silk dyeing, does, on solution in the dye bath, split off a certain amount of nitrous acid, which causes trouble by attacking the copper of the vessels used. It is possible that in the boiling bath a little of the gaseous mixture commonly called nitrous fumes might be driven off into the air to the detriment of the dyer. But the dye for this reason is now usually subjected in its manufacture to a supplementary process whereby the loosely-attached nitroso-group, the source of the trouble, is partly removed and partly destroyed. And it must be noted that in the case of the untreated dye, the trouble is due to nitrous acid, and not to aniline or any compound of that nature.

We have spoken of the impossibility of aniline being already present as free aniline in a commercial solid dye, as rendering the product more or less sticky and easily detectible. The presence of a solid salt of aniline (the hydrochloride or sulphate are the only two which could ever be met with commercially) in the solid dye powder might be considered possible; at least, such a contaminant would not be detectible physically, i. e., inspection or handling the dye would not indicate its presence. But against this possibility we must set two facts. The salts of aniline are very soluble in cold water, and are not capable of being "salted out" of solution as solids by saturation of the solution with common or Glauber salt; whereas this is precicely the way in which water-soluble dyes are gotten out in solid form from the liquid mixture in which they have been produced. Any salt of aniline, therefore, which may have been present in the reaction-liquid in which the dye was prepared, must remain entirely in the waste liquor, and can never appear in the finished dye. In addition (the second fact of the two), if by any accident a finished dye should contain as impurity any solid salt of aniline, this, in the dye bath, would remain definitely in solution, and could not volatilize with the steam of the bath, the salts of aniline being non-volatile, unless the bath were made alkaline, thus setting free the aniline base itself; which then, of course, would pass out into the atmosphere with the steam. Except in the case of physical contact of the person of the dyer with the dye bath, which is not to be expected, only aniline present as vapor in the air can exert its poisonous effect upon the dyer. Dyeing from an alkaline bath is carried on almost entirely in the case of vat dyes alone (which are not silk dyes).

Yet, to deal with this case also, let us consider the vat dyes. These substances are solids insoluble in water, which are furnished to the trade in the form of aqueous pastes, which are put into solution for dyeing by "vatting." This process consists in reducing the insoluble dye with hydrosulphite (as now usually carried out, though a few other reducing agents are sometimes employed), almost always in the presence of alkali. The dyeing from this solution is never carried out at the boil, as far as we know, but only from a hot, warm, or even cold bath. If, therefore, in a vat paste there should be any free aniline or an aniline salt, in spite of the presence of alkali, no aniline could be steamed off into the air, and so no poisonous effect exerted. Now, it is true that in a few cases the "vatting" of the dye, not the dyeing, has to be carried on at the boil, so that here the aniline, if present could escape into the air. But, in the preparation of the vat dyes, the solid product, insoluble in water, let us remember, if washed thoroughly and repeatedly in the filter press to remove all soluble matter originating in the synthesis of the dye; with the result that any aniline salt (or free aniline itself, which is rather surprisingly soluble in water) would be completely and permanently removed before the dye was marketed. This case also must therefore be dismissed as impossible.

Absorption of Dye from Bath

There is one last possible explanation of the erroneous impression with which we are dealing—but so unreasonable that we mention it only because we have endeavored to consider the whole question exhaustively. That is, the accidental poisoning of the dyer by absorption of a dye from the bath, through the skin. (The possibility of aniline here, it will be seen, has already been excluded.) However, the dyer is not supposed to handle the dry dye with his hands, nor is he expected to immerse any part of his body in the dye bath.

We know of a few cases in which a dyer, handling a dry dye with his naked hands instead of using a scoop, has been seriously affected by absorption of the dye through the skin. But such an occurrence is due to gross neglect of the rules of common sense, and should not be ascribed to any danger inherent in the occupation of dyeing, which is no more dangerous than almost any other technical art.

A dye in solid form may, and probably will, exert a toxic or definitely poisonous effect upon the system, if inhailed as dust; and aniline and similar compounds are highly dangerous if either inhaled in vapor form, as in steam from a boiling bath in which free aniline is present, or absorbed through the skin through

being spilled upon the hands or clothing, if not washed off at once. Usually, when aniline poisoning takes place, there is sufficient warning of the danger in the first stages. The symptoms usually noted are dizziness, headache, actual vertigo or reeling, cyanosis (blue lips and face), humming and ringing of the ears, and labored breathing. These symptoms increase in severity, if the person affected does not at once place himself under the care of a physician; and unless promptly treated pass into fainting, coma, and death. The symptoms are characteristic enough not to be confused with those of other classes of poisons. As to poisoning by inhalation of solid dyes in dust form, the symptoms might be almost anything indicating serious physical conditions, though almost always the inhalation of such a substance gives sufficient warning by the provoking of instant and violent sneezing.

From what has been stated, it is evident that there is practically no possibility of poisoning taking place in the dyeing of silk or of any other material, provided the dyer uses ordinary care. This is a requirement in any technical process. Even in the case of gross carelessness, it is difficult to see how poisoning can take place; certainly, aniline poisoning. We have been unable to find any reference whatever to known cases of the sort mentioned in the library and records of the Department of Public Health, of the Harvard Medical School. Altogether, we think it safe to say that any such cases are unknown, and are inherently impossible.

Redyeing

Method, Formula, Temperature, Etc., to Meet Conditions Peculiar to Fabrics Received for Redyeing

THE condition of all types of fabric received for redyeing must at all times be closely observed.

For example, the sunburned (carbonized) condition of wool may not always be visible to the naked eye, yet such damage is further aggravated, or tendering of the fabric increases, in an alkali solution (soda, soap, ammonia, etc.). Experience only will tell the one who is examining the garment the degree to which it has been sunburned, and the safety limits for redyeing.

Oxygen is an important factor in the sunburning, or carbonization, of wool. Then, if the garment has not been too severely sunfaded, it may be treated in a peroxide or permanganate-and-sulphurous-acid bleach prior to dyeing in order to uniformly oxidize the fabric, thus enabling the dyer to secure more even penetration of dyestuff. In order to secure more even penetration of black dyestuff on sunfaded garments of woolen material, some dyers, prior to dyeing, give the garments a treatment with weak javelle water (sodium hypochlorite) followed by careful rinsing.

Dyeing formulas, in general, are based on the handling of new fabric. This fact must be given consideration in the redyeing of garments that have more or less been affected by various agencies during their service, in particular, sunburn, inasmuch as the fabric that has seen service will absorb dyestuff much more rapidly than new cloth.

Salt is added to the dyestuff solution in order to aid in the absorption of dyestuff by the fabric. Glauber salt (sodium sulphate), because of its purity (freedom from iron), is, in general, most adaptable to the dyeing of light shades, while the use of pure common salt is permissible in the dyeing of dark colors. If the percentage of salt is increased above normal (usually 20 per cent) in dyeing, the absorption of dyestuff in the fabric is materially slowed up.

In redyeing sunburned wool it is important to prevent too rapid penetration of the dyestuff. This may be affected by increasing the usual amount of salt and (in case an acid dyestuff is employed) reducing the acid to one-half. Most dyers prefer acid dyestuffs in redyeing sunburned wool.

Temperature

Wool dyes best at the boil (212 deg. Fahr.) when hard water is used; however, the ttemperature may be materially reduced (200 deg. Fahr., or slightly above) when soft water is employed, and a much evener penetration will be secured as well as a much livelier piece of cloth.

Silk is yellowed and furthermore injured at excessive temperature. It should not be boiled. 180 deg. Fahr is most adaptable to silk dyeing.

Cotton or linen, as well as regenerated cellulose (artificial silk, or rayon), dyes best at 150 deg. Fahr. (scalding), allowing the bath to cool down to secure deeper penetration.—Dyers' and Cleaners' Review.

THE CANADIAN COAL TAR INDUSTRY

Production of the coal tar and products industry in Canada was well maintained in 1925, according to a statement recently issued by the Dominion Bureau of Statistics at Ottawa. In that year the output of coal tar distillation plants was valued at $2,502,629 and manufactured disinfectants were worth $120,192, making the total value of the year's production $2,622,821, as compared with the corresponding figure of $2,637,573 in 1924.

Reports were received from fifteen plants in 1925, one more than the number reported in 1924. Of the fifteen establishments classified under this industry in 1925, nine were engaged in the distillation of crude tar to produce such commodities as refined tar, road tar, pitch, creosote oils, protective paints, tarred felts, and sheathings. The six other plants manufactured disinfectant preparations, liquid soaps and insecticides.

Protein Compounds—II

The Isoelectric Point of Various Proteins and Its Relation to Compound Formation—The Keto and Enol Forms of Protein Structure—The Hydrogen Ion Concentration as the Controlling Factor in Compound Formation—The Basicity of the Acids with Proteins

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The Isoelectric Point of Proteins

THE proteins are described by Loeb, "Proteins and the Theory of Colloidal Behavior," Second Edition (1924), page 34, as amphoteric electrotypes which exist in three states, according to their hydrogen ion concentration, namely (*a*) as non-ionogenic or isoelectric protein; (*b*) metal proteinate, as sodium or calcium proteinate; and (*c*) protein-acid salts, as protein chlorides, sulphate, etc.

Now the isoelectric point of a protein or other compound is that point at which the ionization of the amphoteric electrolyte is at a minimum, but it need not be zero in all cases. Where the ionization is at a minimum, the chemical activity is also at a minimum, and therefore it follows that the proportion of protein in combination is also at the lowest point. Very probably the isoelectric point is where the change from the keto to enol form of combination, or *vice versa*, occurs in the protein structure, if such changes do occur.

Loeb states that it is possible, though not proved, that the difference in the behavior of the proteins on the two opposite sides of the isoelectric point is accompanied by an intermolecular change in the protein molecule, and that the protein anion in a metal proteinate may be considered an isomer of the protein cation in the protein-acid salt. Such a possibility is suggested by the action of indicators, the electrolytic dissociation of which is accompanied by an intramolecular change. Miss D. J. Lloyd, *Biochem. J. 14*, 147 (1920), and many others regard it probable that under the action of acids, gelatin goes to the keto form, and under the action of bases, to the enol form.

Loeb, *loc. cit.*, Chapter II, with his classical silver nitrate-gelatin-potassium ferrocyanide experiments shows that the isoelectric point of gelatin is pH 4.7. Speakman, *J. Soc. Dyers and Colourists 41*, 175 (1925), by the same method demonstrated that the isoelectric point of wool is about pH 4.8. Dr. H. C. Chapin of Lowell Textile School in 1925 showed the author a set of wool samples prepared in this manner which very clearly demonstrated an isoelectric range for wool at about pH 4.8. The British Silk Research Association, in British Patent No. 252,064, give the isoelectric point of true silk as pH 3.8.

Csonka, Murphy and Jones, *J. Amer. Chem. Soc. 48*, 763-8 (1926), investigated the isoelectric points of a number of proteins, Table No. XII, and found that a correlation appears to exist between the isoelectric points of proteins of the same group. Thus, the most soluble proteins, albumins, have the lowest isoelectric points, while the less soluble, *a*-globulins, which precipitate with ammonium sulphate at a low saturation, have higher isoelectric points than do the albumins. The isoelectric points of the albumins in general range from pH 4 to 5; the globulins from pH 5 to 5.5; and the prolamins 6 to 6.5. A classification based on isoelectric points would group these proteins in the same way that they are grouped in the classification in use at present.

TABLE XII

The Isoelectric Points of Proteins

	pH
Albumins	
Lactalbumin	4.55
Ovalbumin	4.80
Animal serum albumin	4.70
Albumin from Georgia velvet bean	4.20
Albumin from jack bean	4.20
Albumin from locust bean	5.50
Albumin from wheat bran	4.20
Globulins	
Stizolobin from Chinese velvet bean	5.35
a-Globulin from Georgia velvet bean	5.50
B-Globulin from Georgia velvet bean	5.35
a-Globulin from Cottonseed	5.50
B-Globulin from Cottonseed	5.35
Globulin from locust bean	5.50
Conphaseolin from navy bean	5.20
Phaseolin from navy bean	4.50
a-Globulin from adsuki bean	5.20
B-Globulin from adsuki bean	4.70
Canavalin from jack bean	5.20

Concanavalin from jack bean	5.50
Glycinin from soy bean	4.70
a-Globulin from lima bean	5.50
B-Globulin from lima bean	5.20
Legumin from pea	5.35
Vicilin from pea	5.20
Vicilin from lentil	4.70
Globulin from squash	5.35
a-Globulin from tomato seed	5.20
B-Globulin from tomato seed	4.90
Globulin from cantaloupe seed	5.50
Globulin from walnut	5.20
Globulin from coconut	5.20
Globulin from wheat bran	5.50
Globulin from almond	5.50
Globulin from flaxseed	5.35
Globulin from filbert	5.50
Arachin from peanut	5.35
Conarachin from peanut	4.90
Edestin from hemp seed	5.60
Serum globulin from animals	5.44

Prolamins

Gliadin from wheat	6.45 and 6.50
Prolamin from wheat bran	6.20
Gliadin from rye	6.60
Zein from corn	6.20
Kafirin from kafir	5.90

Miscellaneous

Casein	4.85 and 4.74
Hemoglobin	6.77 and 6.78
Gelatin	4.70 and 7.70

Some Additional Isoelectric Points

Casein (cow)	4.6[1] and 4.7[2] and [3]
Gelatin	4.6[4] and 4.7[5]
Serum albumin	4.7[6]
Serum globulin	5.4[2]
Egg albumin (hen)	4.8[7]
Denatured serum albumin	5.4[6]
Oxyhemoglobin	6.7[8]
Red blood cells	4.6[9]
Yeast extract proteins (globulin)	4.6[10]
Gliadin	9.2[2]
Edestin	5.6[11]
Wool	4.8[12]
Silk	3.8[13]
Callagen (hide powder)	5.0[14] and 4.8[15]

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Ash-Free Silk

In connection with the isoelectric point of the proteins, British Patent No. 252,064, to the British Silk Research Association, W. S. Denham and W. Brash is of interest. The patent covers a process for removing the ash from true silk by treating it with an aqueous solution acidified sufficiently to bring the silk to its isoelectric point (pH 3.8). The patent goes on to state that silk has amphoteric properties, and that in pure neutral water, or in a neutral salt solution, it has very feebly acidic properties and can combine with or fix mineral bases. In order to remove these acidic properties and thus render silk unable to fix mineral bases, a small quantity of acid must be added to the solution, but if more than the requisite amount of acid is added, the silk exhibits basic properties and can combine with or fix some of the acid.

The patent goes on to state that the acid thus fixed is not readily removed by washing with water unless the water is alkaline; but if the alkalinity of the water is due to involatile alkali, or if it is due to a volatile alkali and the water contains mineral salts as does softened water or hard water, the silk will again fix mineral matter and its mineral content, represented by the ash, will not be the minimum attainable. Thus, although the mineral content of silk may be reduced by washing it with water containing a considerable proportion of acid, there is a danger that a deleterious proportion of acid may be left in the silk or, on the other hand, that the mineral content may be raised again if alkali is used to neutralize the residual acid.

They state that the isoelectric point of silk is pH 3.8, and that experiments have shown that if silk is treated with an amount of acid not considerably in excess of that which will bring it into the isoelectric condition, the ash contents are considerably reduced, and the final product is neutral or substantially neutral. This method consists of subjecting silk to the action of water containing acid in quantity sufficient to bring the silk into the isoelectric condition, separating the silk from the water, with or without washing, and finally drying it.

For example, 25 grams of degummed mulberry silk were immersed in 2 liters of distilled water and dilute nitric acid was added until the water contained 0.00063 per cent of free nitric acid (pH 3.7), using Bromophenol Blue as indicator. The silk was removed from the solution after it had soaked for twenty-four hours, wrung out, soaked again for an hour, wrung out again, washed with distilled water, dried and conditioned. The ash before treatment, calculated on the air-dry weight of the

silk, was 0.55 per cent; whereas after the above treatment it was only 0.04 per cent.

Tussah waste was degummed with soap solution, washed with tap water, and 100 grams of the waste soaked for a half hour, with occasional stirring, in two liters of solution *A*. Solution *A* consisted of neutral water (pH 7.0) containing 10 degrees of hardness. Solution *B* consisted of the same water of 10 degrees of hardness but at pH 3.7. A second sample was treated in solution *B*. Both samples were then centrifuged, rinsed twice with fresh quantities of their respective *A* and *B* solutions, and centrifuged after each rinsing. They were then dried and conditioned. The ash content of the Tussah silk treated with the A solution was 1.69 per cent, on the anhydrous silk weight, whereas the ash of the silk treated with the *B* solution was only 0.16 per cent, thus showing the beneficial effect of treating the silk with water and the requisite amount of acid.

Theoretically, the ash content of the silk treated with an acid solution at its isoelectric point should be reduced to zero. The above slight ash content of the treated silk indicates that silk is not one individual protein, but a mixture of more or less closely related proteins which probably have isoelectric points not very widely separated, but which gives the silk an "isoelectric range," rather than a definite isoelectric point.

It is not quite clear to the author just what advantageous properties are possessed by the mineral-free silk but probably it may be in connection with weighting or mordanting, or a better resistance to heat in drying, etc. If mineral-free wool would be desirable for any particular purpose, it would in all probability be possible to obtain it very readily by a process similar to the above, only using water acidified to pH 4.8, the isoelectric point of wool, instead of the above pH 3.7 solution. Obviously it would be impossible to wash this isoelectric wool or silk in the usual aqueous soap solution, or it would immediately combine with sufficient alkali from the soap to bring it in equilibrium with the aqueous solution.

The Hydrogen Ion Factor

The importance of the hydrogen ion concentration in all protein reactions has been stressed in this, as well as all previous papers of this series, and from a consideration of the isoelectric point and the difference in the compounds formed on each side of this point, it is difficult to see how too much emphasis can be given to this factor. In a recapitulation, Loeb, *loc. cit.*, page 21, points out "that in the colloidal literature proteins were assumed to combine by absorption and not stoichiometrically. Because proteins are amphoteric electrolytes and their salts are strongly hydrolyzed, it is necessary to measure the hydrogen ion concentartion of the protein solutions with the hydrogen electrode before any conclusions can be drawn concerning the nature of the combination of proteins. If this is done it is found that proteins react stoichiometrically with acids and alkalies, and that there is no difference between the chemistry of proteins and that of crystalloids." . . . "It is, therefore, obvious that the so-called colloid chemistry of proteins is a system of errors based on inadequate and antiquated methods of experimentation."

Loeb, *loc. cit.*, page 38, describes how on the alkaline side of the isoelectric point all proteins act as if they were entirely or essentially (probably polybasic) fatty acids, due to their carboxyl groups, while the remainder of the molecule is inert. On the acid side of their isoelectric point, the activity of the carboxyl groups is suppressed and the amino groups become active, in which case the proteins behave like ammonia, which according to Werner, "Neuere Anschaunngen auf dem Gebiete der anorganischen Chemie," 3rd Edition (1913), is capable of adding an acid, that is HCl, the H ion of the acid being added directly to the N while the Cl remains outside of the ring in the following manner:

H
HNHCl
H

In Protein Compounds—I, we have just seen how Robertson found that on each successive addition of reagent (acid or base), with the resulting change in the hydrogen ion concentration of the solution away from the isoelectric point of the protein, more and more —CO.HN— groups are combined with the reagent. The extent of this combination is entirely and only a function of the hydrogen ion concentration of the liquor and the isoelectric point of the protein present.

Thus, on any change of the hydrogen ion concentration of the medium surrounding the wool, in either direction away from the isoelectric point of that particular protein (pH 4.8), more of the protein enters into combination with the reagent. As the pH rises above the value of 4.8 (that is, the concentration of hydrogen ions decreases) more wool enters into combination with the base present. As the pH value drops (that is, the hydrogen ion concentration increases), more acid goes into combination with the wool present.

We might just diverge from the main point for a moment to compare this particular fact with the dyeing of wool. On each successive addition of sulphuric acid to the acid dye bath, further color acid is removed from the dye bath and unites with the wool protein. However, we will defer a detailed discussion of this particular point until later.

Loeb graphically portrays these reactions of the proteins at various hydrogen ion concentrations as shown below, in which the inactive portions of the protein molecule is enclosed in brakets. While these show only one amino and carboxyl group, it is certain that more than one amino or imino group is capable of adding an acid molecule, etc.

Isoelectric protein $\begin{pmatrix} —NH_2 \\ R—COOH \end{pmatrix}$.

On the alkaline side (Gelatin pH>4.7) $\begin{pmatrix} —NH_2 \\ R—COOH \end{pmatrix}$.

On the acid side (Gelatin pH<4.7) $\begin{pmatrix} —NH_2 \\ R—COOH \end{pmatrix}$.

Sodium compound $\begin{pmatrix} —NH_2 \\ R—COOH \end{pmatrix} + NaOH = \begin{pmatrix} —NH_2 \\ R—COONa \end{pmatrix} + H_2O.$

Hydrochloride $\begin{pmatrix} —NH_2 \\ R—COOH \end{pmatrix} + HCl = \begin{pmatrix} NH_2HCl \\ R—COOH \end{pmatrix}.$

Further proof of the importance of the hydrogen ion concentration as a factor in protein compound formation is given by the following abstracts:

Pugarsky and Liebermann, *Arch. ges. Physiol. 72,* 51 (1898), stated that when investigated potentiometrically, "the number of Cl^- ions bound by a given mass of protein dissolved in dilute hydrochloric acid is exactly equal to the number of H^+ ions which it binds."

Pauli and Hirschfed, *Biochem. Z. 62,* 245 (1914), found that the combining capacities of normal deaminized gelatin, as well as several other proteins, for acids depended almost entirely upon the ratio of acid to protein, and the maximum amount of acid in combination was not materially affected by dilution of the system. The percentage of combined acid increases as the amount of acid present increases.

Oryng and Pauli, *Biochem. Z. 70,* 368 (1915), found that both normal and deaminized gelatin, in solution in potassium chloride, combined with a definite proportion of Cl^- ions, and that this amount increased greatly upon the addition of acids.

Briggs and Bull, *J. Phys. Chem. 26,* 845 (1922) state that "the taking up of dyes is a case of absorption and that the amount of dye absorbed varies continually with a change in the hydrogen ion concentration of the dye bath." In spite of this fact they continue that "No evidence of chemical action between dyes and wool has been found."

E. A. Valla, *La Concertia 32,* No. 873, 6-11 (1924), writes that the absorption of dichromate by hide depends mostly upon the relative proportions of these present in the bath and the amount of hydrochloric acid present. Hydrochloric acid increases the absorption but damages the leather if too concentrated.

Bogue, "Chemistry and Technology of Gelatin and Glue," page 253, says "that the same amount of chlorine was always in combination with a given mass of gelatin for the same hydrogen ion concentration. This means that if the concentration and hydrogen ion concentration of a gelatin are known, the amount of chlorine in combination with it may readily be calculated. This holds equally well for bases, for at the same hydrogen ion concentration the amount of cation in combination is always the same."

D. Burton, *J. Soc. Leather Trades Chem. 8,* 456-70 (1924), says that the greater concentration of acid will cause a greater fixation of acid by the amino groups of the protein.

W. R. Atkin and G. W. Douglas, *J. Soc. Leather Trades Chem. 8,* 359-70 (1924), report that at pH 1.7 the amount of hydrochloric acid fixed by gelatin rises sharply with decreasing pH. From the isoelectric point (pH 4.7) to 1.7, the curve is rather flatter, from pH 4.7 to 7.7 the amount of sodium hydroxide fixed increases more and more. From pH 7.7 the curve is an almost perfect sigmoid (S shape). A. and D. state that the two sigmoid curves merge into each other between pH 4.7 and 7.7. Titration curves of certain proteins with these reagents have been shown by Harris, *Proc. Royal Soc. B95,* 440-84 (1923), to be sigmoid curves, and from this A. and D. say that 1 gram of gelatin is equivalent to 3.04 c.c. of 0.1 normal sodium hydroxide or an equivalent weight of free carboxyl groups of 3290. Another portion of the curve, pH 7.7 to 12.6, is also sigmoid and represents a combining weight of 2600. There is a keto-enol transformation taking place in this portion. Wilson's second isoelectric point, *J. Amer. Chem. Soc. 44,* 2633-6 (1922), at pH 7.7 is a point of inflection in the above curve and appears to represent the commencement of the introduction of alkali into the —CO.NH— group in which there has been a molecular rearrangement into the enol form =C(OH).NH—, the hydroxyl then combining with alkali.

L. T. Harris, *Proc. Royal Soc. B97,* 364-86 (1925), investigated the combination of proteins, amino acids, etc., with acids and alkalies, and their combining weights. He obtained "pH-combination curves" by plotting the pH values of a protein solution against the alkali (or acid) added, after correcting the latter for the "hydrogen ion error." This correction was made by subtracting from the quantity of alkali (or acid) added, the amount of alkali (or acid) which would have to be added to a hypothetical blank, consisting of water only, in order to produce the same total volume of liquid having the same pH as the amino acid and alkali (or acid) mixture. He found that the amount of alkali or acid (corrected for the blank) required by a protein solution over a given range of pH is proportional to the amount of protein present. For example, the number of cubic centimeters of tenth normal hydrochloric acid (corrected) required to titrate 10 c.c. of milk from pH 6.65 to pH 5.2, is numerically equal to the percentage of protein present. The equivalent combining weights of proteins can be found by adding successive amounts of acid or alkali to the protein and observing a physical constant of the resulting solution. When values of the latter are plotted against the acid or alkali added, the curve shows a sharp break at the point denoting the addition of a constant equivalent of acid or alkali.

In discussing wool as an amphoteric colloid, J. B. Speakman, *J. Soc. Dyers and Colourists 41,* 172-9 (1925), says that wool may be regarded as a typical amphoteric col-

loid, and as such, can combine with either acids or bases, through its amino and carboxyl groups, and the keto and enol forms of its —CO.NH— groups. He shows that the percentage neutralization of wool by acids or bases depends entirely upon the hydrogen ion concentration of the solution. With four varieties of wool he found the combination with hydroferrocyanic acid began at pH 4.8 to 4.9, which he believes to be the approximate isoelectric point. This work coincides very well with that of Loeb. In this paper he also discusses the dyeing of wool, which will be considered under the theory of dyeing.

D. C. Carpenter, *J. Biol. Chem. 67*, 647-58 (1926), investigated the relation of the hydrogen ion concentration of a 1 per cent casein solution to its decomposition at various temperatures. He found that with this particular protein, at 5 deg. Cent. (41 deg. Fahr.) on the acid side of the isoelectric point hydrolysis appears to follow reaction of the first order at a given pH value and bears a simple relationship to pH. On the alkaline side of the isoelectric point the relationship to pH is very complex and is not given on a mathematical basis. His curve suggests that two types of protein compounds are present, one existing above pH 9 and easily hydrolyzed, the other existing below pH 9 and less readily hydrolyzed.

Basicity of Acids with Proteins

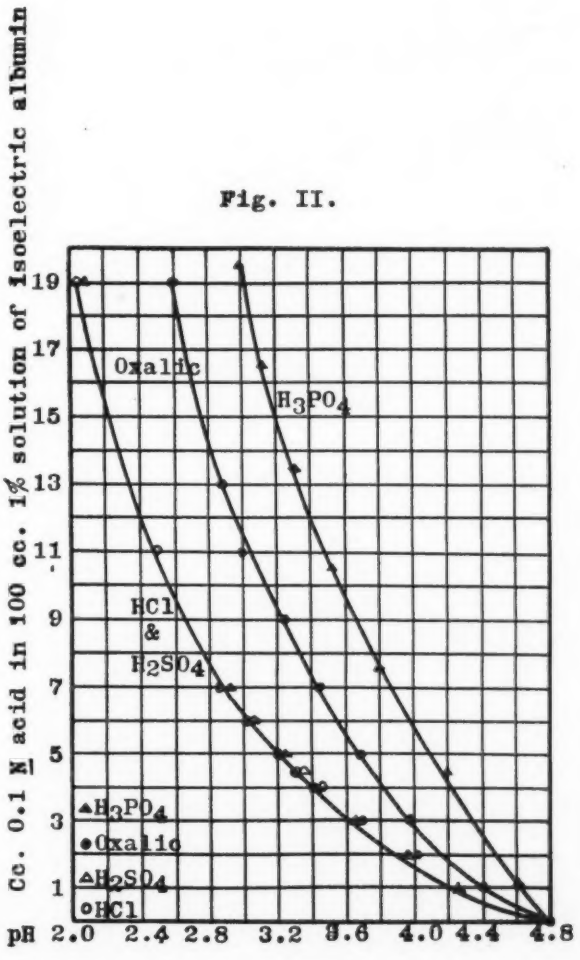
Further quantitative evidence of the formation of protein compounds is given by Loeb's titration curves of the genuine proteins with acids, "Proteins and the Theory of Colloidal Behavior," Chapter IV. Loeb writes that "It can be shown by titration experiments that acids and bases combine with proteins in the same way as they combine with crystalline compounds, namely, by the purely chemical forces of primary valency. It is known that a weak dibasic or tribasic acid gives off one hydrogen ion more readily than both or all three, and that it depends on the hydrogen ion concentration of the solution whether one or two or three hydrogen ions are dissociated from a tribasic acid. Thus, phosphoric acid (H_3PO_4) will give off only one hydrogen ion as long as the pH is below 4.6. Oxalic acid, which is a stronger acid, will act like a monobasic acid below a pH of about 3.0 (also see J. H. Hildebrand, *J. Amer. Chem. Soc. 35*, 847 (1913), while above this pH it acts more like a dibasic acid. In a strong dibasic acid, like sulphuric acid, both hydrogen ions are held with so small an electrostatic force that even at a pH of 3.0 or considerably below the acid acts as a dibasic acid."

Bogue, *loc. cit.*, page 253, states that in oxalic acid the primary ionization is about 760 times as great as the secondary ionization; and with phosphoric acid the primary ionization is about 50,000 times the secondary, which in turn is about 500,000 times the tertiary ionization; while with the stronger sulphuric acid, the primary ionization is only about 33 times that of the secondary ionization.

Loeb continues that if the forces which determine the relation between these acids and proteins are purely chemical, it would follow that three times as many cubic centimeters of O.1 *N* phosphoric acid should be required to bring 100 c.c. of 1 per cent solution of isoelectric gelatin to a given pH below 4.6, for example, pH 3.0, as are required in the case of nitric (HNO_3) or hydrochloric acids (HCl). For the same reason it should require just as many cubic centimeters of 0.1 *N* sulphuric acid as of 0.1 *N* hydrochloric acid. Twice as much 0.1 *N* oxalic acid should be required to bring the isoelectric gelatin solution to pH 3.0 or below as of hydrochloric acid. Figure No. II, by Loeb, shows that these predictions are true.

In this figure, the pH of the solutions are plotted as the abscissae, while the ordinates are the number of cubic centimeters of 0.1 *N* acid required to bring the 1 per cent solutions of originally isoelectric egg albumin (total volume 100 c.c.) to different pH values. The curves represent these titration values for hydrochloric, sulphuric, phosphoric and oxalic acids. Bogue has shown

Fig. II.



that the curve for nitric acid is almost identical with that of hydrochloric acid. These curves show almost identical results for the strong acids, sulphuric, hydrochloric, and nitric. In other words, these three acids combine with proteins in equivalent proportions. On comparing the curve for phosphoric acid with that of the stronger acids, we find that for each pH the ordinate for phosphoric acid is as nearly three times as high as that for hydrochloric acid as the accuracy of the experiments permit. This shows that the phosphoric acid combines with the protein in molecular proportions and that the anion of albumin phosphate is the monovalent anion H_2PO_4. Loeb continues that the values for oxalic acid are for a pH below 3.2, almost but not quite twice as high as those for hydrochloric acid, indicating that for these values of pH oxalic acid combines to a greater extent in molecular and only to a small extent in equivalent proportions with albumin. He also goes on to show that the combining ratios of the four acids named with crystalline egg albumin are the same as those which would be found if we substituted the crystalline ammonia (NH_3) base for the coloid egg albumin.

Loeb carries the stoichiometrical proof of compound formation even further and by means of curves, plotting the cubic centimeters of 0.1 *N* acid in the protein solution against the actual pH value of the solution, he has shown that when acid is added to a given quantity of originally isoelectric albumin or gelatin, at the same pH of the solution equal quantities of hydrogen ions enter into combination with the protein, regardless of whether a strong acid (HCl or H_2SO_4) or a weak acid (H_3PO_4) is added. His results on egg albumin are given in Table XIII. Table XIV shows the same results on gelatin.

These tables show that the proteins combine stoichiometrically with the acid and the simplest assumption is that there is a strictly chemical combination.

TABLE XIII

Cubic Centimeters of 0.1 N Acid in Combination with One Gram of Originally Isoelectric Crystalline Egg Albumin in a 100 c.c. Solution

pH	c.c. of HCl	c.c. of H_2SO_4	c.c. of Oxalic Acid	c.c. of H_3PO_4
4.2	1.15	1.15	1.8	3.8
4.0	1.7	1.7	2.8	5.3
3.8	2.3	2.3	3.7	6.3
3.6	2.9	2.9	5.0	8.6
3.4	3.5	3.5	6.3	10.6
3.2	4.2	4.3	8.0	13.1
3.0	5.0	5.1	9.5	16.1
2.8	5.8	5.9	11.1	19.3
2.6	6.7	6.5	13.3	22.9
2.4	7.6	7.0	16.0	...

"Proteins," Loeb, page 58.

TABLE XIV

Cubic Centimeters of 0.1 N Acid in Combination with One Gram of Originally Isoelectric Gelatin in a 100 c.c. Solution

pH	c.c. of HCl	c.c. of H_2SO_4	c.c. of Oxalic Acid	c.c. of H_3PO_4
4.0	...	2.7	3.9	6.95
3.8	3.9	3.75	5.5	9.4
3.6	4.8	4.8	7.3	12.3
3.4	5.6	5.75	9.1	15.2
3.2	6.4	6.75	11.0	18.0
3.0	7.2	7.5	13.15	20.7
2.8	7.9	8.25	15.3	23.6
2.6	8.35	8.8	17.1	26.2
2.4	8.5	9.3	18.	...

"Proteins," Loeb, page 61.

Loeb also experimented with several acids on casein, and with hydrobromic, hydroiodic, sulphosalicylic, lactic, acetic, and propionic acids on gelatin, while Hitchcock, *Jour. Gen. Physiol. 4,* 597 (1921-2); *5,* 35 (1922-3), obtained titration and combination figures for hydrochloric, sulphuric and oxalic acids upon edestin and serum globulin. All of these figures substantiate Loeb's original work. The titration curves of egg albumin, casein, gelatin, edestin and serum globulin, with 0.1 *N* solution of sodium, potassium, barium, and calcium by Loeb and Hitchcock further substantiate the former work.

If albumin, gelatin and other proteins as well as the amino acids, form compounds with acids or bases, is it not logical that wool also forms these compounds? The existence of such compounds is practically universally accepted by the biochemists as well as many others, and from some of the more recent papers upon leather and tanning subjects, they are rapidly gaining ground in these fields also.

Speakman, *Jour. Soc. Dyers and Colourists 40,* 408-11 (1924) uses the data on the absorption of acids from solutions of various strengths by wool, from the work of Georgievics, Dietl, and Fort and Lloyd, to prove combination of acids with wool in stoichiometrical proportions. In this paper Speakman stresses the chemical combination of the basic dyes with wool.

If sulphuric and other acids unite in stoichiometrically proportions with albumin, gelatin, and wool, why is it not logical to assume that the color-acids of acid dyestuffs also unite chemically with wool and silk in dyeing? The acceptance of these compounds and reactions is certainly a great stride toward the solution or explanation of many rather obscure points in the textile and other related industries. Undoubtedly a wider acceptance of the chemical theory only awaits a better understanding and application of the theories regarding hydrogen ion concentration and the resulting changes in proteins. Loeb, page 57, says that if the relation of the hydrogen ion concentration factor to protein compound formation has been

discovered earlier, "nobody would have thought of suggesting that acids combine with proteins according to the adsorption formual."

(*This is the seventh article in the series of papers relating to Wool by Mr. Mullin. The first paper of the series was published in the* AMERICAN DYESTUFF REPORTER 15, 245-7 (1926). *The next paper, Protein Compounds—III, will appear in an early issue. In this paper the base-protein-acid compounds proposed by various investigators will be discussed and the recent journal literature on protein compounds will be reviewed.*)

CORRECTION

An unfortunate omission occurred in printing the article Protein Compounds—I, by Charles E. Mullin, in the issue of August 23. The paragraph from which a line was omitted was near the bottom of the second column on page 534, and should have correctly read:

"Among a large number of more or less common amphoteric compounds, that is, compounds having the property of exhibiting either basic or acidic properties, depending upon the conditions to which they are *subjected, aluminum hydroxide serves as an excellent example. We are* all more familiar with the composition of this inorganic compound than that of the complex proteins, and Bogue ('Chemistry and Technology of Gelatin and Glue,' page 220) gives an excellent discussion of amphoteresis in connection with it."

The italicized passage was omitted.

Hydrogen Ion Concentration and Its Application to Textile Industries

By E. R. TROTMAN, Ph.D., B.Sc., A.I.C.

(*Abstract*)

IT has been known for a long time that the activity of an aqueous solution of an acid or a base is proportionate to concentration of the hydrogen or hydroxyl ions. Thus, the vastly different activities of N/10 hydrochloric and N/10 acetic acids, both of which give the same values when titrated with a standard solution of an alkali, are entirely due to the difference in the degrees of dissociation when the two acids are dissolved in water.

In the past one has been restricted to such unsatisfactory terms as "faintly acid" or "strongly alkaline"' in the description of the reaction of a solution. Such terms do not convey any definite information, and their interpretation is largely a matter of personal judgment. It was a great advance, therefore, when a scale was suggested by which the activity of an acid or alkaline solution could be measured quantitatively.

Pure water dissociates into hydrogen and hydroxyl ions to a small but definite degree—

$$H_2O <—> H^+ + OH^-$$

Since this reaction is reversible, the product of the concentration (C) of the hydrogen ions and that of the hydroxyl ions will be constant. That is to say—

$$C_H \times C_{OH} = K$$

In neutral water $C_H \times C_{OH} = 10^{-7}$.

When an acid is added to water, the hydrogen ion concentration is increased and the hydroxyl ion concentration is proportionally diminished, so that the product of the concentrations of the two ions may remain constant. When an alkali is added, exactly the reverse occurs. That is to say, the hydrion concentration is diminished proportionally to the number of hydroxyl ions present. Thus, the concentration of the hydrogen ions is a measure not only of the acidity of a solution but also of the alkalinity.

The actual hydrion concentrations are very small and not convenient for everyday use. Therefore the *p*H values are used, these being the logarithms of the concentrations of the hydrogen ions with their signs changed from negative to positive. The relation between the normality of a solution of a fully dissociated acid or alkali, its hydrogen ion concentration and the *p*H value is as follows:

Normality with respect to H Ions	Actual H Ion Concentration	*p*H
N/1	1	0
N/10	0.1	1
N/100	0.01	2
N/1,000	0.001	3
N/10,000	0.0001	4
N/100,000	0.00001	5
N/1,000,000	0.000001	6
N/10,000,000	0.0000001	7
N/100,000,000	0.00000001	8
N/1,000,000,000	0.000000001	9
N/10,000,000,000	0.0000000001	10
N/100,000,000,000	0.00000000001	11
N/1,000,000,000,000	0.000000000001	12

The *p*H values of a few common solutions are given below:

HCl		NaOH	
N	0.10	N	14.05
0.1 N	1.07	0.1 N	13.07
0.01 N	2.02	0.01 N	12.12
0.001 N	3.01	0.001 N	11.13
0.0001 N	4.01		
CH_3COOH		NH_4OH	
N	2.37	N	11.77
0.1 N	2.87	O.1 N	11.27
0.01 N	3.37	0.01 N	10.77
0.001 N	3.87	0.001 N	10.27

Measurement of *p*H *Values.*—The *p*H values are measured either by colorimetric methods or electrometrically.

Colorimetric Methods are described by Evers (Analyst, 1921, 46, 393). Every indicator changes color at a characteristic *p*H value, as shown in the table below:

Indicator	*p*H Range over which it changes
Thymol Blue	1.0— 3.0
Brom-phenol Blue	3.0— 4.5
Methyl Red	4.5— 6.6
Brom-cresol Purple	5.0— 7.0
Brom-thymol Blue	6.0— 8.0
Phenol Red	7.0— 8.5
Phenolphthalein	8.5—10.0
Thymolphthalein	10.0—11.0

The solution is tested with these indicators in turn, till one is found which gives with the solution a tint intermediate between its two extreme colors. This shows the approximate *p*H value of the solution, and a series of solutions are prepared from buffer mixtures having accurately known *p*H values in the neighborhoods of the rough value first found, until one is obtained which gives a shade which exactly matches that obtained with the liquid being tested.

Solutions of known *p*H value cannot be prepared by dilution of acids or alkalies, since very small changes in concentration cause large variation in the hydrogen ion concentration. The difficulty may be avoided by addition of acids or alkalies to so-called "buffer" solutions. These generally contain salts of weak acids which tend to reduce the variations of *p*H liable to be caused by small alterations of conditions. Such solutions are described by Evers (*loc. cit.*). The universal buffer solution of Prideaux and Ward (J. C. S., 1924, 125, 426) is useful, and is sold by the British Drug Houses, Ltd.

Mixed indicators give continuous color changes over fairly large ranges of *p*H values. They are described by Evers (*loc. cit.*), and one of the most useful is the British Drug Houses Universal Indicator, which gives a continuous range of color changes between *p*H values of 3 and 11.

Electrometric Methods are much more accurate, but require elaborate apparatus. A relatively simple apparatus is described by Monier-Williams (Analyst, 1921, 46, 315). When a bar of metal is immersed in water, ions go into solution, with the result that the metal becomes negatively charged and the water positively charged. A potential difference is therefore set up between the metal and the water which rapidly attains a constant value. When the water already contains ions of the metal, however, the tendency for the metal to lose ions is decreased by the tendency for the solution to deposit them. The potential difference will, in consequence, be smaller, and the diminution will be proportional to the number of similar ions originally present. Hydrogen, absorbed on platinum black, behaves in exactly the same manner, and the potential difference may be used as a measure of the number of hydrogen ions present.

The E.M.F. of a single electrode cannot, however, be measured accurately, and it must be combined with another electrode giving a known and constant E.M.F. Such a cell is the calomel electrode, which contains mercury in contact with a saturated solution of calomel. Potassium chloride must be added to the calomel solution to increase the conductivity, and the calomel is therefore dissolved in either N/10, N/1, or saturated potassium chloride solution. Formerly the N/10 cell was most commonly used, but since the E.M.F. changes with alterations in the concentration of the potassium chloride it has been found that the saturated cell is less liable to give rise to variations due to this cause.

The E.M.F. of the cell formed by the hydrogen electrode combined with the calomel electrode must be measured. This is done by the Poggendorf compensation method, or more conveniently by the Hilderbrant method, in which the E.M.F. of the cell is read directly on a millivoltmeter.

The *p*H of the solution may then be calculated with the aid of the following equations:

(1) Using an N/10 calomel electrode—
$$V = 0.366 + 0.0591\ pH.$$
(2) Using an N/1 calomel electrode—
$$V = 0.284 + 0.0591\ pH.$$
(3) Using a saturated calomel electrode—
$$V = 0.245 + 0.0591\ pH.$$

In which V is the E.M.F. of the combined cell.

Electrometric Titration.—It is frequently extremely difficult to titrate colored solutions, since the color masks the change of the indicator. Such a solution can be titrated readily with an electrometric apparatus for determination of hydrogen ion concentration. The calomel and hydrogen electrodes are immersed in the solution, and acid or alkali is run in, with constant stirring, till the E.M.F. corresponds with that of a neutral solution.

Application of Hydrogen Ion Concentration to Textile Industries.—The most important application is, perhaps, the determination of the nature of an acid or an alkali in

a textile fabric. It is frequently necessary to find if cotton has been tendered with a strong acid. The fact that an acid reaction is obtained with indicators is not conclusive proof, since this may be due to harmless organic acids. Further, the fact that the aqueous extract gives the qualitative reactions of mineral acids is also valueless as a rule, since salts of these acids may very well be present. If, however, the *p*H of the aqueous extract be determined and the strength of the acid in terms of normality be then found by titration, one may establish definitely whether the acid be a weak or strong one. Thus it is known, for example, that an N/100 solution of hydrochloric acid has a *p*H of 2.02, and an acetic acid solution of the same strength has a *p*H of 3.37. In just the same way the nature of an alkali may be determined.

Determination of Acidity or Alkalinity of a Dye Liquor.—Cases occasionally occur when it is necessary to determine whether a dye liquor be acid or alkaline, and also how much of either is present. Titration with an indicator will be impossible on account of the color of the dyestuff. It is impossible, as a rule, to discharge the color of the solution without altering its reaction. Since electrometric titration dispenses with the necessity of an indicator, this will obviously be a case in which it will be especially serviceable.

The relation between the adsorption of acids and dyestuffs by wool and the *p*H of the solution has been discussed recently by Speakman (this Jour., 1924, 40, 208; 1925, 41, 172), Reinmuth and Gordon (Ind. Eng. Chem., 1923, 15, 818), and Briggs and Bull (J. Phys. Chem., 1922, 26, 845) have also shown that the *p*H of the dye liquor is an important consideration in dyeing with acid dyes.

S. R. Trotman and E. R. Trotman in a recent paper read before the Midlands Section (this Jour., 1926, 42, 154) described the importance of controlling the *p*H of hydrogen peroxide bleaching solutions if the best result is to be obtained with the least amount of damage and loss of weight. The *p*H of bleaching powder solutions is also an important factor in cotton bleaching, but unfortunately neither the electrometric nor the colorimetric methods give very reliable results with solutions of hypochlorites

The measurement of hydrogen ion concentration is rapidly becoming of increasing importance. Further, the use of *p*H values should be of the greatest assistance to those concerned with the finishing of textile fabrics. For example, it is much easier to arrange to have a peroxide bleaching liquor made up to a *p*H of 9.5, with the aid of a suitable mixed indicator, than to have it merely made faintly alkaline, when the actual alkalinity will be different every time the bath is made up.—Journal of the Society of Dyers and Colorists.

Turkey-Red Oil and Its Competitors

Prime Materials for Their Production—Methods of Sulphurating—Neutralization of the Sulphurated Oil

By H. POMERANZ

TURKEY-RED OIL is a thick water-soluble oil (sometimes the aqueous solutions are opalescent and show a more or less milky opaqueness) obtained by sulphurating castor oil, and by mixing the sulphurated product with a determined quantity of alkalis. In most cases the oil possesses the character of an acid soap; entirely neutral products are not very often placed on the market. Consequently the characteristics of the commercial Turkey-Red oil are:

1. The prime material, castor oil.

2. The pre-treatment with sulphuric acid, provoking an essential alteration of the oil.

3. The neutralization of the sulphurated product, effecting the complete solubility in water.

These three characteristics can be changed, and from these alterations result various products not only capable of replacing in many cases the usual Turkey-Red oil, but even surpassing it. These substitutes are to be described and characterized in this article.

If one mixes the castor oil with conc. sulphuric acid, the mixture becomes warm and dark-colored, then, congealing, it yields, when fixed with water, an opalescent, nearly transparent, solution. After addition of caustic ammonia or alkalis, it becomes clear and transparent. The reaction between the oil and the acids is accounted for by the supposition that the ricinoleic acid, which in the carbon atom ring has combined a carbon atom with a hydrosilicic group, is esterified by the sulphuric acid according to the equation—

$$\begin{array}{l} R\ldots CH(OH)—CH_2—CH_2\ldots CH{=}CH—CH_2\ldots + H_2SO_4 \\ \qquad\qquad\qquad\qquad\quad = R\ldots CH(OSO_2H)—CH_2\ldots + H_2O \end{array}$$

In the presence of the group SO_3H the oil becomes water-soluble. At the same time a partial saponification of the castor oil, eliminating the glycerine, takes place. But this theory may be objected to by the fact that sulphuric acid ester has never been reproduced in pure state, nor has it been analyzed. Consequently, the existence of this ester is only a speculation, accounting for the reaction between castor oil and sulphuric acid Sulphuric acid also reacts with other oils and fatty acids

—*i. e.*, with olive oil and oleic acid. This reaction is considered as a fixation of sulphuric acid to the double combination of the unsaturated sebacic acid; this supposition, however, may also be applicable to ricinoleic acid. Moreover, Henri Schmied sulphurated coconut oil and used it in alizarin dyeing instead of Turkey Red oil. As the principal amount of fatty acids contained in this oil is the myristine acid, a saturated fatty acid of the series of acetic acids, the reaction between this fat and the sulphuric acid — unless it should be caused by the tenor of unsaturated fatty acids—is supposed to be a simple saponification.

Leaving out of the question the theoretical explanation of the sulphurating process, let us adhere to the fact that any fat showing a rise of temperature with the so-called Maumne's trial undergoes an alteration when treated with sulphuric acid. This alteration also becomes manifest in the soap proceeding from the corresponding sulphurated product, and the fat is serviceable for certain technical purposes not until it has been subjected to this pre-treatment. The nature of this alteration is supposed to be colloid-chemical, and this supposition means that, in spite of the chemical character of the salts and the esters, etc., the combinations proper do not exist, as the definite laws of constant proportions are missing. Even the soaps which are justly considered as salts, cannot pass for soaps in a strict sense of the word, as in aqueous solutions they do not only decompose into acid salts and free alkali, but they yield variable acid salts, whose composition depends upon the temperature and concentration of the solution. Therefore, it would be a mistake to regard these combinations of the oil with sulphuric acid, being far less fast to water than soaps, as chemical combinations. Pure fatty acids combine with sulphuric acid only if they are oxifatty acids or unsaturated fatty acids; the quantities of sulphuric acid combined with the fatty acid vary considerably; even the minimum amount of sulphuric acid is sufficient for effecting the combination of oil and water, and the combination with water is the chief characteristic of the sulfo-sebacic acids.

A similar process may be observed with other colloids —*i. e.*, with starch. The character of the glue is altered even by the least amount of certain substances contained in the starch. One often speaks of salts, esters, etc., of starch, but those must not by any means be considere as chemical individuals, which we know. On the contrary, the combinations occurring here are called adsorptive in colloidal chemistry.

The natural fats constitute a mixture of various fatty acids, among which are also unsaturated fatty acids. They are glycerine esters of these fatty acids, and are subject to the action of sulphuric acid with regard to saponification as well as to formation of ester. Chemical technics generally use castor oil for the sulphurating process, as it contains an unsaturated fatty acid. It is very expedient for sulphurating, but nearly all saponifiable fats and oils may undergo the same process by means of sulphuric acid.

Methods of Sulphurating

The amount of sulphuric acid which remains combined with the sulphurated oil is not distributed all over the oil. It is combined only in some form or other with a portion of the sulphurated product, whereas the remainder is saponified either not altered at all by the sulphuric acid, or eliminated only from the glycerine. In this respect the sulphurating process resembles the esterifying process. The fatty acid esters have no fastness to water: if the sulphurated mixture is poured into water, free sulphuric acid is eliminated. A great portion of this sulphuric acid has been eliminated from the sulfoleate by means of water. Extremely small quantities of combined sulphuric acid in the oil are sufficient to maintain the character of the so-called sulfoleate of the oil. Concerning the composition of the sulfo-sebacic acid there exists a rich literature containing technical and chemical explanations about the subject.

The results of all the investigations with regard to Turkey Red oil may be summarized in the fact that as yet chemical science has not succeeded in accounting for the alteration of the oils by means of sulphuric acid, the sulphurated products being characteristic colloids, which cannot be produced in a pure analyzable state. With reference to technical results, the conclusion has been arrived at that in most cases the partially neutralized sulphurated oil could be replaced by the corresponding acid soap of the same oil. In Turkey Red and para-red dyeing, and in the finishing process, the Turkey Red oil has long ago been replaced by acid ricinoleic soap.

There is a marked difference between the Turkey Red oil and acid ricinoleic soap, especially with reference to the insolubility in water. The Turkey Red oils have a far higher solubility than the ricinoleic soaps, which are the most soluble among all sebacic alkalis. Also the insoluble metallic soaps of the Turkey Red oil differ from those of the castor oil: the magnesia soap is more soluble, and the lime soap is oily and settles to the bottom, etc. Also, the free sulphurated fatty acid is soluble in water to a certain degree, with the result that the sulfo-sebacic acids have a certain degree of fastness to acids, etc.

In consequence of these properties the sulphurating of oil is an advantageous pre-treatment which has been preserved up to the present time in the technical operations of the oil industry. Though the Turkey Red oil has lost its importance for dyeing and finishing, it has kept its high value as a soaking agent, as a soap more compatible with acids, lime, and magnesia than any other. Owing to its acid nature, which is very advantageous for leather, the Turkey Red oil is still made use of in tanning.

As soon as these properties of the Turkey Red oil show themselves, the sulphurating process must be executed in such a manner that greatest possible amount of sulphuric acid remains combined with the oil. By

working under certain conditions one can accomplish the sulphurating process with sulphate of chlorhydrin SO_3HCl instead of hydrate of sulphuric acid SO_3H_2O. In this case the water and glycerine must be precluded, as they would decompose the chlorhydrin. The chlorhydrin separates hydrochloric acid, whereas the sulphuric acid anhydrin combines itself with the fat.

The sulphurated product is poured into water, in which it is dissolved completely clear and crystallized. One obtains a solid, granular product, clearly soluble in water, soluble in dilute mineral acid and in concentrated pure acetic acid and formic acid, giving no precipitate with dilute magnesia solution, in lime solution an oil heavily settling to the bottom, thus completely complying with the requirements concerning fastness to acids, lime, and magnesia. Owing to the entire preclusion of water, the sulphuration with chlorhydrin can be accomplished more energetically without involving an oversaturation—i. e., a rupture of the carbon ring of the fatty acids. Thus one obtains liquid products entirely soluble in a saturated solution of common salt, equally in sodium hydrate of 5% to 30%, and whose fastness to acids, lime, and magnesia is superior to that of the previously mentioned solid sulphurated product.

The sulfoleates produced by means of chlorhydrin seem to be identical with the water-soluble part of the Turkey Red oil, which has been insulated by Scheurer-Kestner. These compounds are not fit for the clearing process of Turkey Red and para red, but they can be used as soaking agents in dyeing, mercerization, etc.

Their large-scale production, requiring the dilution of the chlorhydrin by means of an organic solvent, is not realizable in consequence of the present conditions in Germany. If this production should ever be possible, they could substitute the sulphurated soaps, as monopole soap, turco oil, etc., which only partially comply with requirements. The later products are castor oil (glycerides) sulphurated with the aid of sulphuric acid, and only a small portion of their substance has been converted into the water-soluble form.

The degree of the action of the sulphuric acid upon the castor oil, according to former statements made by Herbig,* is in direct proportion neither with the quantity of the acid nor with the duration of the action; but the method of treating ulteriorly the mixture, and especially the way in which it is washed, is a factor of great importance to be reckoned with. As already mentioned, the washing operation effects the decomposition of the sulfofleate in oil free from sulphuric acid (coxi-sebachic acid?) and sulphuric acid (sulphur dioxide?). In a neutral or concentrated, weakly alkaline solution, the oil containing sulphuric acid is much more constant. One takes advantage of this circumstance for maintaining the maximum possible part of sulphuric acid in the oil: the sulphurated mixture is neutralized with sodium hydrate, and the sulfoleate soap freed from the sulphate of soda. This is accomplished in any way, either by means of crystallizing the latter or by the separation of the sulfo-sebacic acid (or, rather, of its acid salt) by decomposing the neutralized sulphurated mixture with weak acid. In this way the decomposed action of water is obviated and the sulphurated product is maintained richer in sulphuric acid. Those compounds are fast to acid, lime, and magnesia. The common Turkey Red oil is washed with water with addition of common salt or sulphate of soda, which it separates from the aqueous solution. By this process a certain amount of alkali penetrates into the oil forming a hydrochlorate of sulfo-sebacic acid. The formation of these constant chemical combinations, as common salt and sulphate of soda, by a weak fatty acid is to be explained in the same way as the formation of soda soap by means of crystallizing a potash soap with common salt: the less readily soluble combination is eliminated from the solution in the process of crystallizing and precipitating. This alkali seems to be combined only with that part of the sulphurated mixture which contains the sulphuric acid, and thus it offers the possibility of decomposing the Turkey Red oil into two compounds, water-soluble parts and water-insoluble parts. The sodium salt is hardly soluble in ether, whereas the free fatty substance of the water-insoluble portion of the ether is easily and entirely dissolved in ether.

The sulphurated oil is kept free from sulphuric acid by boiling it with dilute acid. It loses its solubility in water, but it is no longer the original castor oil, nor ricinoleic acid. It has been converted into dixistearic acid, which in the form of soap is used for Turkey Red and para-red dyeing. Also monopol-soap and similar castor oil compounds can be used instead of the ordinary Turkey Red oils.

The Neutralization of Sulphurated Oil

The sulphurated oils, as well as the unsulphurated oils, yield soaps soluble with alkalis but insoluble with heavy metals. The water-soluble portion of the Turkey Red oil, respectively, the portions sulphurated with sulphate of chlorhydrin, give soluble magnesia soaps. The insoluble soaps generally are oily, which is a valuable factor with lime soap, as it settles to the bottom as a heavy oil, making the water nearly entirely free of lime. This is the meaning implied by the expression "fastness to lime."

The alkaline soaps mostly in use are soda soaps

*Lehnes, "Farber-Zeitung," vol. 1892, 1894-96.

and ammonia soaps; potash Turkey Red oils are used more seldom. If the Turkey Red oil is washed with sodium salt, it absorbs, as has been previously mentioned, soda, so that if the neutralization process with ammonia is continued, a mixed soap is obtained. Pure ammonia Turkey Red oil is obtainable only from unwashed, respectively, uncrystallized, oils. Sulphurated oils which have been neutralized in a high degree, and especially castor oils, are clearly soluble in water. Less neutralized oils give opalescent solutions, and even more or less opaque emulsions. The grade and the nature of the neutralizing process are of the greatest importance for particular purposes: for alizarin red the ammonia Turkey Red oil is the most suitable. Sometimes it contains also a certain addition of peroxide of tin (for clearing process). For para red, where it is added to an excess of caustic sodium, the neutralization is of no importance. As soaking oil, finishing oil, etc., it is used in the form of its acid sodium salt. The monopole soap owes its consistence, sometimes also its action, to the high-degree neutralization with sodium. The grade of neutralization is unimportant for the fastness to acids. On the other hand, it is more advantageous, for solutions containing magnesia, to employ the oil in an entirely neutral state and combine the magnesia with the fatty acid, as hydrochlorate and sulphate of magnesia crystallize the oil.

Recapitulation

The common Turkey Red oil is a castor oil sulphurated with concentrated sulphuric acid, 25% of its weight. The castor oil, after having been washed and crystallized from the aqueous solution with the aid of common salt or Glauber salt, is neutralized in a certain degree with sodium or ammonia. Varations in this method can take place with regard both to the original material and to the method of sulphuration and neutralization. One can produce a range of fat compounds which, according to the application, can completely replace the Turkey Red oil in one direction or another. For Turkey Red and para-red dyeing common ricinoleic soaps with a high percentage of fatty acids are preferable to Turkey Red oil; the same applies to most cases where Turkey Red oil is used for clearing or brightening colorations. A sulphurated product obtained without having been washed is as a soaking agent superior to Turkey Red oil (monopole soap, tourko oil, etc.). The same products are used for finishing purposes. According to the degree of neutralization one obtains liquid, half-solid, and solid products, soluble in water, sometimes clear, sometimes turbid, very often of different behavior when used.

In general one must always take into account the fact that the soaps produced from sulphurated fats have a different character from those produced from fats which have not previously been sulphurated. Thus the sulphuric acid treatment brings forth a range of new original materials for soap manufacture. The actual conditions are such as to preclude the application of castor oil to chemical practice, and it will be a task in conformity with the present need to produce the necessary compounds also from other oils; these compounds should have the same technical action as those produced from castor oils. It is an incontestable fact that in textile technics castor oil can be whooly replaced by other oils. — "Leipziger Monatschrift," translated by The Textile Manufacturer.

TESTS FOR MERCERIZED MATERIAL

The tests for distinguishing between ordinary and mercerized cotton have been fairly satisfactory in the past, but a certain amount of skill has been required in making the test, even where Lange's test was employed. In the Linen Industry Research Association publication R. W. Kinkhead maintains that the tests originally suggested by Knecht and Knaggs did not command confidence, generally speaking, since different materials required differing amounts of acid to make the distinction clear. He holds that his test is very simple and reliable.

A small cutting of the material is soaked in a cold solution of a 0.001 per cent solution of Methylene Blue, to which has been added 0.5 per cent sodium carbonate.

The stained material is then washed lightly with distilled water and covered with about 10 c.c. of a 3 per cent solution of sodium carbonate at the bottom of a test tube. Four drops of a 1 per cent iodine-in-potassium-iodide solution are then added and the lot heated to the boil. The solution is then poured off and immediately replaced by fresh cold-water solution.

Mercerized material becomes reddish-purple, while unmercerized material acquires a blue or bluish-green shade.

The test has been utilized for testing whether a linen material has been treated with caustic soda solution of a density not less than 40 deg. Tw.

Further, the approximate strength of the soda used for the treating of the material may be estimated by comparing with a range of samples of known treatment strengths.

Where material has been mercerized with concentrated mineral acids, a different behavior is to be seen from that mercerized with alkali, a result which, in conjunction with the iodine test, makes it possible to distinguish these materials.—Textile Argus.

Brown Mahon, vice-president of the Judson Mills, Greenville, S. C., will in the future divide his time between the mill and New York sales department.

AMERICAN
DYESTUFF REPORTER

Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

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THE DYER KNOWS

HOW much of the trouble in dyeing rayon can be traced to the purchasing department of the mill only the dyer knows. He will agree, nevertheless, that it is unfair to expect the purchasing agent to be as well informed as himself about the technical properties of the various rayons on the market. It is not within the province of the purchasing department to be expert in the selection of dyes, chemicals and soap. These are usually tested by the laboratory. It certainly follows that rayon—most fickle of fibers—should be bought with the same scrupulous care.

And yet, we repeat, most rayon processing troubles have their origin in the purchase of rayon on a price basis or on the strength of its appearance only, and this the dyer knows well. He knows that all rayon looks very much alike to the purchasing agent, but he has learned by many bitter experiences that in this case looks are indeed deceiving. Into his dyehouse comes a new shipment of rayon, presumably only two kinds. In the dye bath its true character is revealed: that which should have been left unstained in the fabric design emerges beautifully intermingled in color with the dyed wool or cotton, as it may be; while the rayon that should have dyed like the other fibers is seen to be not one kind but two, or perhaps three.

It is obviously an occasion for profanity and it is hardy surprising, unfair though it may be, that the weight of it falls upon the dyer. Yet he knows what caused the trouble; he knows that three or four kinds of rayon were purchased when only two were desired, and he also knows that *he* could have selected the proper rayon with little difficulty and could have saved the energy consumed in damning him, not to mention other economies. Yet with this knowledge in his possession he is content to work along under the severe disadvantage of never knowing in advance what freakish effects his dye bath will cast forth, never knowing what dyes to order, because he cannot know what type of rayon will next appear in his dyehouse. It seems to us that his position in such a case is one of grave responsibility and that he is open to a charge of incompetency if he does not explain the situation to the purchasing department. He is even justified in going a step further than mere explanation if that fails. Were he to demand that he be consulted in the buying of rayon it is possible that his mill would recognize the evil of its ways and grant his rights.

BENEATH TRADE-MARK AND GUARANTEE

TIME was when the public was fooled part of the time into buying dyed fabrics which were labeled "fast" but which belied the epithet when introduced to soap-suds or sunlight. Intensive advertising and educational publicity have taught the consumer to look for trade-marked fabrics and fastness guarantees supported by the reputation of reliable manufacturers. The place of the trade-mark in textile merchandising is now fully recognized, a fact attested to by the publication of a directory listing not less than twenty-five thousand trade-mark names for textile products. The consumer—usually in the person of the housewife—has her attention called to these branded fabrics through magazine and newspaper advertising and soon finds by trial the brands that have a fastness suited to her requirements. By a natural process of selection and rejection those of inferior color endurance are slowly but surely weeded out and in the press of competition they soon drop by the way.

It was not so long ago that all dissatisfaction caused by fugitive colors was directed at American dyes. At first, during the infant days of our dye industry, as we all know, it was the custom to reply to these charges with a promise of better dyes to come. But when our industry did start to produce genuine fast dyes in a range of shades broad enough to satisfy any reasonable demands and it was seen with some chagrin that these were not immediately appreciated and that baseless accusations of inferiority continued with the deathless persistence of intentional propaganda, our dye manufacturers frequently lost patience — and rightly so. They retorted in a tone that plainly said "What more do you want? You asked for fast dyes; here they are. They may cost a little more, but in the long run they are worth it."

That is all history, but not the sort of history that Henry Ford called "bunk." Now, more than ever before, fast dyes are indeed worth every penny of their difference in cost. The responsibility for fastness has shifted to the textile manufacturer, for the consumer knows that fast colors can be obtained, knows that guarantees can be made, knows who makes them, and buys accordingly. To-day the demand for washable, non-fading fabrics

must be met by trade-marked brands and fastness guarantees.

The textile manufacturer who pays a few cents more per pound for his dyes, who employs skilled dyers and chemists in order to be sure those dyes are applied properly, who sends his goods into the market with a guarantee, and backs that guarantee with an advertised name stamped on the selvedge, practically insures the popularity of his products. But if he credits his success entirely to the trade-mark and the guarantee he is unreasonable. If he did not use the fast dyes—for which, remember, he pays only a few cents more — his guarantee would be a scrap of paper, his trade-mark a sham.

A LESSON IN INDUSTRALISM

NO longer can the I. G. be considered solely as a dye cartel. Its manufacture of dyes is now but slightly more than half of its pre-war production and forms only a portion of its interests. Through its numerous amalgamations with other industrial units, its activities have spread like a vine, with tendrils fastened to a score of inter-related industries. It has become a chemical trust of incredible dimensions—chemical in the broadest sense of the term. The concise review of its current fusions by Trade Commissioner Daugherty in this issue gives us an enlightening picture of this giant which " occupies a towering position" in German industry.

The close of the war saw the I. G.'s important dyestuff markets held firmly by foreign competitors. Dye factories had been set up in several countries to fill the urgent need for war chemicals. But as America, England, France and Switzerland secured their independence in dyestuff manufacture, they waged commercial war among themselves for the trade of China, Japan and other Eastern markets. The Germans, with enviable foresight, realized that the overthrow of their monopoly had created severe competition among the dye producers of every nation and they planned immediately to regain their former power through other channels, knowing well that their leadership in the dye trade was irrecoverable.

Their *modus operandi* constituted a series of moves that were strokes of commercial genius. By foreign agreements which removed tariff barriers, by price reductions which shut out competitors in some export markets, by mergers of their foreign sales agencies, by consolidations at home which brought new sources of raw materials under their control, they have climbed to a position which dwarfs their former eminence. Their recent entrance into the field of cellulose products, metal alloys, fertilizers and fuels on a large scale and their close relations with two of the biggest explosive concerns in Germany gives them important and profitable outlets for their tremendous manufacturing capacity. Dyestuff manufacturing alone, they found, is insufficient to support their costly plant facilities.

The secret of their success has been cartelization. They have taken into their fold every industry that was in any way related to their numerous enterprises. The consequent control of all necessary raw materials, the specialization in manufacture by the various members of the combination and the absence of practically all competition at home offers a text from which American industry may draw some instructive lessons. Although cartelization is to some extent illegal in this country, the mutual confidence which must underlie it is not prohibited and wherever that exists the benefits have been numrous. If we cannot have a trust we can at least have trust.

SCIENTISTS DISCUSS DYE RESEARCH

At the recent meeting of the British Association for the Advancement of Science at Oxford, England, an interesting paper on the value of abstract research in the field of dyestuffs was delivered by Professor J. F. Thorpe.

He stated that no fundamental advance in the chemistry of dyestuffs had been made since Bohn discovered Indanthrene in 1901, although great advances had been made in the preparation of new colors belonging to this and other known series. But at any moment one or other of the men or women engaged in fundamental research might repeat Bohn's discovery of 1901 and obtain a new compound which will be the forerunner of a new series of dyestuffs.

The portion of his address which dealt further with this subject was as follows:

"It is perhaps too much to ask in an industry which is struggling to hold its own to expend large sums on the prosecution of abstract research, most of which will be of no use to it, but it is not too much to expect that the industry will take every means to foster and encourage abstract research in our university institutions, and even to give some lead as to the direction in which its experience leads it to think that advances may be made.

"There is at present no organization which can bring the manufacturers of dyestuffs and intermediates into touch with the work being carried on in our university laboratories, and it is possible that if at the present time a valuable discovery were to be made it would be unrecognized as such, and, following the usual course of academic research, would be published, and thus lost to the country. What is required is a lead from manufacturers which will indicate the matters which they regard of importance, but which they do not consider as likely to yield results sufficiently quickly to justify them in employing their own research staff for investigating them."

GERMAN-JAPANESE DYE AGREEMENT REPORTED

The commercial treaty between Germany and Japan recently concluded provides for the removal of Japanese import restrictions against German dyes, according to a cable from Tokio. A tacit agreement has been entered into whereby non-competitive colors only will be shipped into Japan from Germany.

It is further said that imports of American dyes are not affected by the terms of the agreement. Dyes from America and other countries have heretofore enjoyed full priviliges, license restrictions having operated only against German colors.

THE DYE TRADE IN AUSTRALIA

Australian tanners are complaining of the restrictions on the importation of dyes. They state that they are prepared to pay the duty (10 per cent), but the procedure which has to be followed involves much delay.

The Australian manufacturer must apply to the Customs Department for permission to import any dyes not of British origin. The customs authorities then determine whether or not a British equivalent is obtainable, and if such is the case permission to import is refused. The British dye agent is then requested to supply the equivalent; which, of course, entails more delay.

Local buyers of dyes are accordingly urging the customs officials to allow them the same privileges enjoyed by purchasers of dyes in other dominions, where, although a duty is levied, the freedom to buy in any market is retained.

ANILINE DYES IN ESTHONIA

The imports of aniline dyes into Esthonia amounted to 210,000 pounds in 1924, a decrease of nearly 33 per cent from the 1923 total of 320,000. Germany's share of this trade fell off proportionately, but continued to make up the bulk of the total importation. The United States did not figure in the trade of either year.

PRATT ALUMINI OUTING

The annual outing of the Pratt Institute Chemical Alumni Association will take place this year on Saturday, September 11, at Fuhrer's American House, Park and Casino, First Avenue and First Street, College Point, Long Island.

The committee assures all members that a good time is in store for those participating in this annual event. In addition to a wonderful dinner, dancing and cabaret there is a very full sports program and several features which are reserved as surprises.

DU PONT STOCK SHARES DOUBLED

At a recent meeting of the directors of the E. I. du Pont De Nemours & Company the annual dividend rate on the common stock was raised from 10 to 14 per cent, on the basis of 3½ per cent quarterly, and a recommendation was made to split up the stock two for one. A meeting was called for Sept. 13 to vote on the proposal to change the authorized common stock from 1,500,000 shares at $100 par value to 5,000,000 without par. Each share of common stock outstanding will be exchanged for two shares of the new no-par common stock. The action, it was learned, came about as a result of the recent declaration of 50 per cent stock dividend by the General Motors Corporation, in which the Du Pont organization owns a quarter interest.

FREDERICK E. ATTEAUX

After a brief illness, Frederick E. Atteaux, president of F. E. Atteaux & Co., Inc., died at his home in the Chestnut Hill section of Brookline, Mass., on August 25, at the age of seventy-four.

In the passing of Mr. Atteaux the American dye industry has lost one of its best known men. For the past fifty years he had been prominent in civic and commercial affairs in Boston, and during his long connection with the dyestuff trade his name was well-known outside of that city.

He was born in Lennoxville, Quebec, and was graduated in 1871 from Bishop's College.

When he first came to the United States he engaged in the dry goods business in Lawrence, Mass., and then went to the dry goods firm of Jordan, Marsh Company in Boston. As a seller and buyer of dry goods, he studied the dyestuffs problem from the angle of the production of effects that would please the public. His next work was as a dyestuffs salesman, and then in 1887 he entered the dyestuffs business for himself in the firm of F. E. Atteaux & Co., which in 1901 became F. E. Atteaux & Co., Inc., with himself as president and general manager. He remained in these positions until his death.

All through his career he was an enthusiastic supporter of the principle that America should produce its own dyestuffs. At the same time he was a keen student of European conditions, and made frequent trips abroad in connection with his business interests. The company owns factories in several States.

He was a member and first president of the Drysalters' Club of New England, and also a member of the Algonquin Club, the Boston City Club, the Engineers' Club, and the Boston Athletic Association. He was a member of the Boston Lodge of Elks. He is survived by his widow, Caroline Willard Atteaux, whom he married forty-one years ago.

INQUIRY DEPARTMENT

All classes of chemical work or advice relating to artificial colors, natural dyestuffs, dyewoods, raw materials, extracts, intermediates, crudes, or dyeing chemicals and accessories in general, will be carried out for readers and subscribers of the AMERICAN DYESTUFF REPORTER by this department.

Inquiries of a minor character will be answered on this page, while major matters involving personal investigation, analyses, perfected processes and working formulas, will, if desired, be treated confidentially through the mails. In answering inquiries which, by their nature, require reference to the products, processes or apparatus of some particular manufacturer we aim to be absolutely impartial. We refer the inquiries to specialists whom we believe to be best qualified to answer them intelligently, and must disclaim responsibility if their reports show unintentional bias. All questions, materials for analysis or letters leading to the opening of negotiations for special work will receive prompt attention if addressed to Inquiry Department, American Dyestuff Reporter, 90 William Street, New York City.

M. J. M.—Question: Kindly furnish me with a practical formula for giving a luster to woolen yarn, particularly carpet yarns. I should also appreciate information on the treatment applied to many Oriental rugs to give them sheen or luster. What I have in mind particularly is the luster on a Chinese Oriental rug. These rugs, I understand, are treated after weaving in such a manner that the ends of the tufts or piles are given a sheen that ordinarily comes to an Oriental rug only with age.

Answer: In regard to carpet yarns, we believe that if you will soak the yarns before dyeing in a bath containing two and a half to three per cent of sulphuric acid and allow this solution to dry in thoroughly before proceeding you will find that the desired luster has been obtained.

In regard to a treatment for Chinese rugs we suggest the following:

Brush the surface thoroughly with a two per cent soap solution, then brush twice with warm water and once with cold water. When the surface has been thus cleansed and rinsed thoroughly with a one per cent solution of sulphuric acid and allow the rug to stand for about two hours, then brush twice with cold water and allow to dry.

Another process which we understand has a similar effect involves treating the completed rug first in a bath containing caustic soda and then in a bath containing Javelle water. We are unable to give the exact procedure or percentages in this latter case, but believe that some experimentation would demonstrate what is the best practice.

A. D.—Question: Will you kindly advise me of a dischargeability test that would give the same effect as produced in the print works?

Answer: The goods are first dyed or printed—usually dyed. A paste is made consisting of 5 to 20 parts hydrosulphite (quantity depending on depth of shade of cloth, darker shades requiring more than light); 50 parts thickening—gum tragacanth or neutral; one-eighth part oxalic acid; remaining parts water.

This paste is brought to 100, then applied to the rollers of the machine. The goods are run through it, then dryed and steamed.

There are, of course, any number of color discharges possible as well, made by mixing the above paste with the desired shade, providing the color selected stands the effect of hydrosulphite.

RECENT LITERATURE

Ciba and Cibanone Colors.

Chlorantine Fast Colors—2 vol. Society of Chemical Industry in Basle.

With an ever-increasing number of color cards being issued both here and abroad—and with America receiving a goodly supply of those from abroad—it becomes proportionately difficult to put out a card that will be both distinctive and more useful than the average. The production of shade cards, in other words, has become an art, upon which often depends the popularity of the particular brand of colors they display.

The Society of Chemical Industry has succeeded exceptionally well in the publication of these three cards, one showing the Ciba and Cibanone colors and two displaying the Chlorantine Fast Colors. The cards are finely bound in cloth and in general make-up are extremely attractive; as reference books for the dyehouse they are without doubt of unusual value, in that the swatches for any group of shades can be quickly located, and because all information pertaining to the class of colors treated is very fully presented in each card.

The Ciba and Cibanones displayed on swatches in three percentages cover a complete range of shades. The text of the card deals very thoroughly with their application, methods of dyeing, of oxidizing, of developing, etc., even to giving concisely in tabular form the preparation of the stock vats and dye vats for each specific shade. Other tables give the fastness properties of each dye for practically every color-destroying agency.

Of the two cards devoted to the Chlorantine colors, that showing this series on viscose is especially attractive, containing 144 swatches in a range of hues running through golden yellows, oranges and violets to the more somber shades of blue, green and black. The last pages exhibit thirty-six shades especially fast to light. Formulas are given for every shade and dyeing instuctions supplied in a brief note in the text.

The Reduction Products of Azo Dyes

Part XX

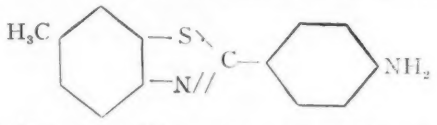
By WALTER C. HOLMES

Color Laboratory, Bureau of Chemistry

[EDITOR'S NOTE.—*The most practical and effective method for the identification of azo dyes consists in the isolation and identification of the products which they yield on reduction. This method finds less application than it might or should, partly because some of these products have never been isolated and investigated, and partly because much of the data which has been obtained in regard to such reduction products is greatly scattered and very difficult to locate.*

Mr. Holmes has made a search for all the available information on such reduction products, and this series contains a digest of his results with a systematic listing of the reduction products of the azo dyes published in the Colour Index, together with the available data on such properties and reactions as would be of service in their identification.]

No. 254.—DEHYDROTHIO-p-TOLUIDINE



$C_{14}H_{12}N_2S$; Mol. Wt. 240.24; (C, 70.0%; H, 5.0%; N, 11.6%; S, 13.3%).

Derived from C. I. Nos. 126, 127 and 128.

Glittering yellow needles (alc.), mpt. 190-1° (also reported as 185°), bpt. 434°. Sol. in 20,000 parts boiling H_2O, sp. sol. in cold alc., readily sol. in Ac HO. Alc. sols. fluoresce violet-blue.

On ignition with zinc dust it yields p-toluidine.

Heated with S it yields primuline base and evolves H_2S. With nitrous acid it gives a phenol, needles (alc.), mpt. 255-6°, alk. sols. of which fluoresce blue.

Its salts are sp. sol. in general and unstable in H_2O. *Picrate,* mpt. 204-6°; *chlorplatinate,* decomposed at 230-40°.

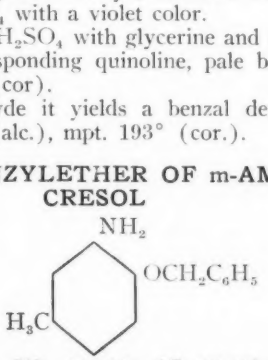
Acetyl deriv., small prisms (alc.), mpt. 225-7°, sp. sol. in Ac HO, nearly insol. in alc.

On diazotization dehydrothio-p-toluidine yields a brown-yellow insol. product, mpt. 270° and a sol. product, mpt. 139°, which may be coupled with (alk.) β-naphthol yielding an azo dye, crimson needles, mpt. 214°, sol. in H_2SO_4 with a violet color.

Heated in conc. H_2SO_4 with glycerine and arsenic acid it yields the corresponding quinoline, pale brown cryst. (alc.), mpt. 147° (cor).

With benzaldehyde it yields a benzal deriv., yellow needles or plates (alc.), mpt. 193° (cor.).

No. 255.—BENZYLETHER OF m-AMINO-p-CRESOL

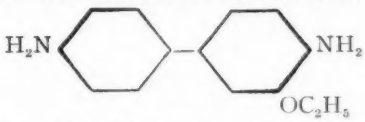


$C_{14}H_{15}NO$; Mol. Wt. 213.20; (C, 78.8%; H, 7.1%; N, 6.6%; O, 7.5%).

Derived from C. I. No. 121.

No data are available but the ether could be identified by conversion into the corresponding phenol. The latter (3-amino-4-cresol) cryst. in rhombic cryst. from ether, mpt. 135°. Sublimes readily. Nearly insol. in H_2O, readily sol. in alc. Sols. of the hydrochloride are colored red by $FeCl_3$.

No. 256.—3-ETHOXYBENZIDINE



$C_{14}H_{16}N_2O$; Mol. Wt. 228.21; (C, 73.6%; H, 7.1%; N, 12.3%; O, 7.0%).

Derived from C. I. Nos. 488 to 493.

Glittering flat needles, mpt. 139° (also reported as 135°). Sp. sol. in H_2O or ether but readily sol. in hot alc. The sulfate forms colorless prisms, sp. sol. in H_2O but readily sol. in HCl with the formation of the hydrochloride.

4'-acetyl deriv., small white leaflets (H_2O), mpt. 137-8°, insol. in ether but sol. in hot H_2O or in alc.; *diacetyl deriv.,* small white needles (alc. or Ac HO), mpt. 240°, insol. in H_2O.

The ether is converted into the corresponding phenol, mpt. 185°, by heating with HCl under pressure.

No. 257.—DI-o-ANISIDINE (Dianisidine)

$C_{14}H_{16}N_2O_2$; Mol. Wt. 244.21; (C, 68.8%; H, 6.6%; N, 11.5%; O, 13.1%).

Derived from C. I. Nos. 494 to 525 and 571 to 577.

Colorless leaflets which become colored violet soon in air. Mpt. 131-2° (also reported as 137°). Soluble in 24 parts boiling H_2O and 90 parts H_2O at 20°. Readily sol. in organic solvents or dil. mineral acids.

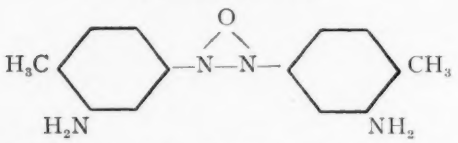
Hydrochloride, prisms, readily sol. but yields a sp. sol. basic salt on boiling in H_2O; *sulfate,* needles, sol. in about 21 parts boiling H_2O but nearly insol. in cold H_2O; *benzene sulfonate,* mpt. 277°, sol. in 47.4 parts H_2O at 18°; *α-naphthalenesulfonate,* mpt. 272°, sol. in 357 parts H_2O at 15°; *β-naphthalenesulfonate,* mpt. 290°, sol. in 1,000 parts H_2O at 15°; *2, 7-naphthalene disulfonate,* mpt. 318°, very sp. sol.

Acetyl deriv., white nodules ($+H_2O$) from water, melts at 67°, loses its H_2O at 100° and then the anhydrous comp. melts at 116°; *diacetyl deriv.,* colorless prisms, mpt. 231°, insol. in H_2O or ether, sp. sol. in alc., mod. sol. in Ac HO or acetone; *dibenzoyl deriv.,* colorless prisms, mpt. 236°, insol. in H_2O and only sp. sol. in alc.

Additive comp. with: *Sym. trinitrobenzene,* flat black needles, mpt. 144°; *1, 3, 6, 8-tetranitrobenzene,* black pdr., mpt. 205°.

Diazotized and coupled with: *β-naphthol,* dark plates with green reflex (toluene), mpt. 310°, green-blue sol. in H_2SO_4, violet pptte. on dil.; *Naphthol AS,* dark violet cryst. pdr. (toluene), mpt. 320°, green-blue sol. in H_2SO_4, blue-violet pptte. on dil.

No. 258.—3, 3'-DIAMINO-4, 4'-AZOXYTOLUOL (Azoxytoluidine)



$C_{14}H_{16}N_4O$; Mol. Wt. 256.23; (C, 65.6%; H, 6.3%; N, 21.8%; O, 6.3%).

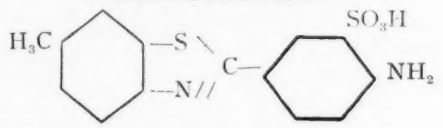
Derived from C. I. Nos. 604 and 605 by partial reduction.

Yellow needles or orange prisms, mpt. 168°. Sp. sol. in H_2O, readily sol. in alc. or ether.

Hydrochloride, small colorless needles, insol. in alc. or ether. It is readily sol. in H_2O but only sp. sol. in presence of salt or excess HCl.

Diacetyl deriv., mpt. 290°.

No. 259.—DEHYDROTHIO-p-TOLUIDINE SULFONIC ACID



$C_{14}H_{12}N_2O_3S_2$; Mol. Wt. 320.30; (C, 52.5%; H, 3.8%; N, 8.7%; O, 15.0%; S, 20.0%).

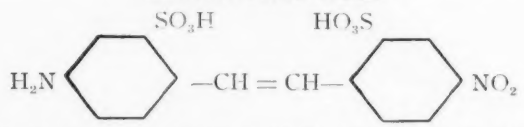
Derived from C. I. Nos. 220 to 226, 632, 634 and 635

Yellow needles ($+1H_2O$) or orange leaflets ($+2H_2O$), nearly insol. in cold H_2O, alc. or ether. Its salts fluoresce blue. It yields a sp. sol. yellow diazo comp. stable even in boiling H_2O.

NH_4 salt ($+H_2O$), small silvery white plates which turn yellowish on drying, sp. sol. in cold H_2O.

Na salt, yellow pdr. readily sol. in H_2O. Treated with NaOCl it yields Chlorophenine Y (Col. Index No. 184). *Cu salt,* brown-red, insol.

No. 260.—4-AMINO-4'-NITROSTILBENE-2, 2'-DISULFONIC ACID



$C_{14}H_{12}N_2O_8S_2$; Mol. Wt. 400.30; (C, 42.0%; H, 3.0%; N, 7.0%; O, 32.0%; S, 16%).

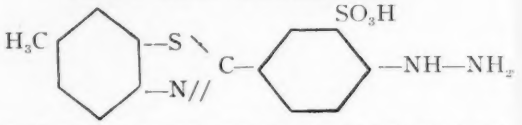
Derived from C. I. Nos. 620 (note), 622 and 624 by partial reduction.

On further reduction it yields diaminostilbene disulfonic acid (see No. 262) and on oxidation with $KMnO_4$ it yields p-nitro-o-sulfobenzaldehyde.

The normal salts are readily sol. in H_2O and are deeply colored (red-brown).

Acid Na salt, small yellow needles, sp. sol. in H_2O. Its diazo deriv. is insol. in acids but sol. in alkalies.

No. 261.—DEHYDROTHIO-p-TOLUIDINE SULFONIC ACID HYDRAZINE

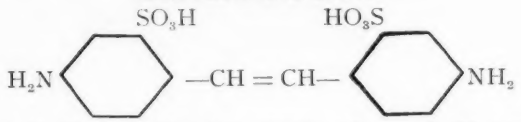


$C_{14}H_{13}N_3O_3S_2$; Mol. Wt. 335.32; (C, 50.1%; H, 3.9%; N, 12.5%; O, 14.3%; S, 19.1%).

Derived from C. I. Nos. 43 and 426 by incomplete reduction.

No data available.

No. 262.—4, 4'-DIAMINOSTILBENE-2, 2'-DISULFONIC ACID



$C_{14}H_{14}N_2O_6S_2$; Mol. Wt. 370.32; (C, 45.4%; H, 3.8%; N, 7.6%; O, 25.9%; S, 17.3%).

Derived from C. I. Nos. 358 to 366 and 620 to 635.

Microscopic yellow needles, insol. in alc. and ether and nearly insol. in H_2O. Readily sol. in alkalies. It gives a microcryst. sp. sol. tetrazo comp. which gives a violet dye with R-salt.

By deamination and alkaline fusion it may be converted into stilbene, mpt. 124°.

It yields p-amino-o-sulfobenzaldehyde on oxidation with (neutral) $KMnO_4$ which gives a deeply colored hydrazone with phenylhydrazine.

On oxidation with alk. $K_3Fe(CN)_6$ it yields a red dye which dissolves in conc. H_2SO_4 with a dark blue color and gives a dark brown pptte. on dil.

The diacetyl deriv. (yellow cryst. pdr., insol. in H_2O) and its salts are phototropic. They turn purple-red in sunlight and return to their original light yellow color in the dark.

No. 263.—o-TOLIDINE DISULFONIC ACID

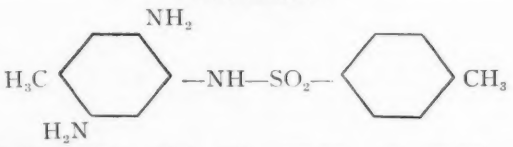
$C_{14}H_{16}N_2O_6S_2$; Mol. Wt. 372.33; (C, 45.1%; H, 4.3%; N, 7.5%; O, 25.8%; S, 17.2%).

Derived from C. I. No. 487.

Small white needles (H_2O), readily sol. in hot H_2O. The tetrazo deriv. is insol. in H_2O.

The salts are readily sol. in H_2O and are easily crystallized. *Na salt* ($+4H_2O$), cubes; *Ca salt* ($+5H_2O$), silvery glittering leaflets resembling mica; *Ba salt* ($+3H_2O$), needles.

No. 264.—2, 5-DIAMINO-4, 4'-DITOLYLSULFONAMIDE

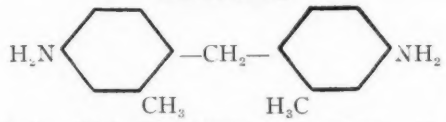


$C_{14}H_{17}N_3O_2S$; Mol. Wt. 291.29; (C, 57.7%; H, 5.9%; N, 14.4%; O, 11.0%; S, 11.0%).

Derived from C. I. No. 107.

No data available.

No. 265.—4, 4'-DIAMINO-2, 2'-DITOLYL-METHANE

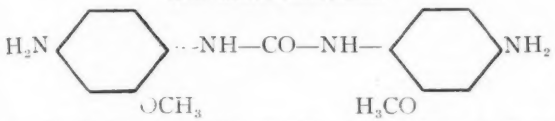


$C_{15}H_{18}N_2$; Mol. Wt. 226.24; (C, 79.6%; H, 8.0%; N, 12.4%).

Derived from C. I. No. 355.

Crystallizes from hot H_2O in colorless needles, mpt. 123°. The hydrochloride is readily sol. in H_2O but diffic. sol. in dil. HCl. Aqueous sols. of the hydrochloride are colored deep violet by warming with $FeCl_3$.

No. 266.—4, 4'-DIAMINO-2, 2'-DIMETHOXY DIPHENYLUREA

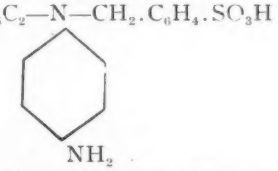


$C_{15}H_{18}N_4O_3$; Mol. Wt. 302.25; (C, 59.6%; H, 6.0%; N, 18.5%; O, 15.9%).

Derived from C. I. Nos. 349 and 349A.

No data available.

No. 267.—ETHYLSULFOBENZYL-p-PHENYLENEDIAMINE



$C_{15}H_{18}N_2O_3S$; Mol. Wt. 306.30; (C, 58.8%; H, 5.9%; N, 9.1%; O, 15.7%; S, 10.5%).

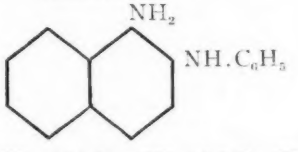
Derived from C. I. No. 42.

The acid and its salts are very soluble and difficult to isolate. May be obtained in the form of its Ba salt.

In acid solution with zinc chloride and sodium thiosulfate it is oxidized by bichromate to a thiosulfonic acid which reacts with α-naphthylamine hydrochloride to form a difficultly sol. dark green indamine dye.

Ethylsulfobenzylaniline may be condensed readily with benzaldehyde yielding Guinea Green B.

No. 268.—2-PHENYLAMINO-1-NAPHTHYL-AMINE



$C_{16}H_{14}N_2$; Mol. Wt. 234.21; (C, 82.0%; H, 6.0%; N, 12.0%).

Derived from C. I. No. 439.

Clear transparent flat prisms or broad needles (alc.), mpt. 136-7° (also given as 138-40°). Insol. in H_2O but readily sol. in hot alc. The amine becomes colored violet in light and its sols. are colored red-violet by oxidizing agents.

Hydrochloride, long glittering colorless needles (Ac HO + HCl) which become colored light violet on long standing. Very sp. sol. in H_2O. In Ac HO sol. it gives brown-red flocks with $FeCl_3$.

On heating with PbO, or on treatment with diazobenzene sulfonic acid, it yields naphthophenazine, citron-yellow needles and prisms (benzene), mpt. 142.5°. The hydrochloride in Ac HO sol. yields a diazoimide with nitrite, thick white needles (alc.), mpt. 149-50° (also reported as 143-4°). The same product is obtained from the base by treatment with isoamylnitrite.

With $COCl_2$ it yields 2-phenylnaphthyleneurea, long prisms (alc.), mpt. 238°.

On heating with benzaldehyde it yields 2-phenylbenzal-1, 2-naphthylenediamine, yellow prismatic needles (alc.), mpt. 138°.

Papers of the Dye Division, American Chemical Society

Presented at the Society's Annual Meeting at Philadelphia, September 6-10

THE Division of Dye Chemistry of the American Chemical Society will hold two meetings this week in connection with the long-heralded Golden Jubilee of American chemists at Philadelphia. The first will be in Bennett Hall on Tuesday, September 7. At this meeting general technical papers on dye chemistry will be heard, abstracts of which are given below. The second meeting, on Thursday, will be featured by a symposium on "The Progress of the Dye Industry in the United States During the Past Decade." Abstracts of some of the papers in this symposium also appear below.

At the general meeting of the society on Monday, September 6, an address will be delivered by Irenee du Pont on "The Dyestuffs Industry, Forerunner of What?"

Several papers of interest to textile chemists are on the program of the Division of Water, Sewage and Sanitation Chemistry, to be covered at its meeting on Wednesday morning in Bennett Hall. These papers are:

Foster Dee Snell and Cyril S. Kimball. Chemical Treatment of Trade Wastes. III—Optimum Conditions for the Removal of Color (Lantern.)

W. E. Hadley. Some Experiences in the Practical Disposal of Trade Waste Produced in the Mercerizing, Bleaching, and Dyeing of Cotton Material.

W. Rudolfs. Effect of Temperature on Sewage Sludge Digestion.

Stuart E. Coburn. Practical Application of Hydrogen Ion Control in the Digestion of Sewage Sludge.

A. S. Behrman. Recent Developments in Zeolite Softening.

J. W. Sale and C. H. Badger. Effect of Chlorination on Sanitary Chemical Analysis of Water.

Edward S. Hopkins. The Effect of Slightly Alkaline Tap Water Upon Spawn and Eggs of Trout and Perch.

A. M. Buswell. The Strength of Soap Solutions Used for Rating Zeolite Softeners.

SYMPOSIUM:

The Progress of the Dye Industry in the United States During the Past Decade

Chairman—Dr. M. L. Crossley

1. Ten Years of Progress in the Dyes and Intermediates Industry in the United States. M. L. Crossley.

2. Importance of Research in the Dye Industry. C. G. Derick.

3. Relation of the University to the Dye Industry. E. Emmett Reid.

4. Protection for the American Dye Industry. Grinnell Jones.

5. The Development of Synthetic Anthraquinone. Kenneth H. Klipstein. (*a*) *The Anthracene Process.* Efforts to develop the anthraquinone vat dye industry demanded a source of supply to anthraquinone. Only one process had found general application on an industrial scale, the chromic acid oxidation of anthracene. Among other steps in the process, the preliminary purification of the anthracene and the recovery of the by-product chromium sulphate after oxidation were outstanding difficulties which would have had to be met by the American manufacturer. (*b*) *Chemistry of the Synthetic Process.* 1877 marked the discovery by Friedel and Crafts of the use of anhydrous aluminum chloride in promoting reaction between certain types of organic compounds. By the use of this catalyst phthalic anhydride and benzene reacted to give orthobenzoyl-benzoic acid, which could easily be condensed to anthraquinone. Later Heller and Schulke determined the ideal conditions under which orthobenzoyl-benzoic acid could be produced by this method. Dr. Gregg Dougherty explains that reaction together with T. M. Lowry's ideas concerning intramolecular ionization. The aluminum atom in aluminum chloride having only six electrons in its outer shell, tends to share two electrons belonging to some other atom or molecule, as benzene or an aliphatic chloride, which becomes polarized or internally ionized. Neutralization follows, with elimination of hydrogen chloride and the formation of, for example, a homologue of benzene. A detailed application of the theory to the information of ortho-benzoyl-benzoic acid is included. (*c*) *Commercialization of Synthetic Anthraquinone.* The difficulties inherent in the anthracene process, together with the availability of phthalic anhydride and anhydrous aluminum chloride, as a result of the development of Gibbs' air oxidation process for the anhydride and of certain processes for the chloride, made it inevitable that the American industry should turn to synthetic anthraquinone. A brief description of the steps of the process follows.

6. The Manufacture of Indigo in America. Charles J. Strosacker.

7. The Progress in the Development and Manufacture of Vat Colors in America. O. M. Bishop and J. H. Sachs. A brief account is given of the development and manufacture of vat colors in America from the early beginning up to the present time. The difficulties encountered and the chief obstacles which for a time retarded progress are pointed out and the main factors which have contributed largely to the overcoming of these obstacles and to successful development and manufacture are discussed. A section is devoted to the reduction of the colors to a physical state suitable for use in the various forms of application in the trade. A resume is given of the different types of vat colors now produced in America, some specific brands are mentioned, and a few pertinent points in connection with their synthesis and manufacture are noted. Finally, a brief perspective is taken of the future problems and prospects of this important branch of the dyestuff industry in this country.

8. The Development of the Food Color Industry in the United States. W. C. Bainbridge. The use of coloring matters in foodstuffs is an old established practice, having originated in the workshop of nature. Man in his endeavor to meet the culinary requirements of advancing civilization found it necessary to perpetuate the familiar and characteristic hues that have suffered deterioration in the process of cooking or preserving. Thus the art of tinting our food products was established. At first the juices of such vegetable products that lent themselves readily to extraction and concentration were employed. With very few exceptions these coloring matters were readily decomposed and the results were far from satisfactory. The advent of coal tar colors brought the desired shades and hues and they soon found a wide application in this direction. The indiscriminate use of those products without thought to their purity or toxic properties forced government legislation in 1907 that resulted in the adoption of the "Certified List of Permissible Food Colors." From the year 1907 to 1914 the production of these colors consisted primarily of the purification of crude dyestuffs of German origin. The advent of the World War terminated this order of things and the manufacturers of these products were called upon to meet the herculean task of production from domestic basic raw materials. Only intermediates and dyes of the highest possible state of purity could be considered. American ingenuity and perseverance did not falter and the result was that the crisis was squarely met. The industry was placed on a firm foundation and can now boast of a greater and superior line of products of truly American manufacture.

9. Medicinals and Dyes. E. H. Volwiler.

10. The Aniline Dyes in Medicine. John W. Churchman.

11. The Production of Biological Stains in the United States. H. C. Conn.

12. The Contribution of the Dyestuff Industry to

the Development of the Rubber Industry. D. H. Powers. The importance of organic compounds as "accelerators" for the vulcanization of rubber has increased tremendously in the past ten years. The dye industry at first supplied intermediates for these organic accelerators, later manufactured some of the accelerators themselves, and now is not only furnishing practically all of the intermediates and some of the most widely used accelerators, but is also developing new and more active accelerators. A recent development is the prevention of the deterioration of rubber by the addition of organic "antioxidants." A study has been in progress of the effect of organic compounds on the rate of aging of rubber, and a product is now being supplied which prolongs the life of rubber goods many fold. Previous to the adaptation of organic dyestuffs to use in rubber products, a very limited number of inorganic colors were available. With this development of dyestuffs, a wide variety of shades, using relatively small percentages, and stocks of superior physical properties, may be obtained. Not only is the dyestuff industry developing further uses for organic compounds; it maintains thoroughly equipped research laboratories which offer to the rubber industry technical advice and service in all lines.

13. The Contribution of the Color Laboratory to Industry. H. T. Herrick. Includes a brief history of the color laboratory, an outline of its more important achievements, and a statement of its future policy.

14. The Work of the Bureau of Standards on Dyes. William D. Appel. The application of spectrophotometry of dye problems is a dominant feature of the work which includes the study of methods of evaluation, standard fastness tests, and other technical problems. Studies of chemical and physical relationship are an important part of the project. Dyes of known purity have been prepared and standard spectrophotometric transmission measurements of their solutions in a number of solvents have been made, measurements which are not only useful in the identification and analysis of the commercial products, but which constitute a fundamental standardization of the types. The relationship between spectral transmission and chemical constitution of certain simple azo dyes has been studied quantitatively. The practical use of the spectrophotometric method for the commercial evaluation of dyes has been shown by comparisons with the titanous chloride titration and the usual dyeing test. A dyeing method which is strictly quantitative and reproducible as well as more rapid than the usual commercial method has been developed. Work on fastness to washing and fastness to light has been done in co-operation with the American Association of Textile Chemists and Colorists with the expectation that methods which are standard for all concerned with dyes and dyed materials will be established.

15. Fur Dyeing and Fur Dyes in America. W. E. Austin. Prior to 1915, 90 per cent of the dyed furs used in this country were dyed in Europe, and such furs as were dyed here were treated with German dyes. To-day, the situation is almost reversed: about 95 per cent of dyed furs used here are American-dyed furs, and the domestic fur dyeing industry is virtually independent of Europe for fur dyes. The consumption of coal tar derivatives for fur dyeing come to $1,000,000-$1,500,000 annually, comprising a range of about forty different individual dyes, as compared with about six ten years ago. Every color of the spectrum is represented, and the chemistry of the reactions is a highly complicated one, quite analogous to the aniline black reactions. American chemists and engineers have succeeded in developing the fur dyeing industry in this country, so that to-day it leads the world in efficiency, modern organization, progressive ideas as to production of new and novel effects in the application of coloring matters to furs. The field is young, and offers great opportunities from the viewpoint of the chemist.

Dye Division Program—Regular Meeting

1. The Effect of Phosphates on the Adsorption of Orange II Dye by Iron, Aluminum and Chromium Gels. (Lantern) Neil E. Gordon and C. E. White. At the Washington meeting of the A. C. S. we reported that phosphates increased the amount of basic dye taken up and decreased the amount of acid dye taken up by inorganic gels. Since that time we have carried out experiments with the object of finding the exact role of the phosphate with the acid dye. We have concluded that the phosphate radical combines with the metal of the gel and forms a compound more insoluble than the metal dye compound. In comparing the effects of the presence of HCl, H_2SO_4 and H_3PO_4 on the taking up of Orange II by iron, aluminum, and chromium gels, we find that H_3PO_4 cuts down the amount taken up unless it is used in large quantities. The reason for this is that the function of the HCl and H_2SO_4 is to dissolve the gel and thus furnish metal ions, which react with the dye and form the insoluble metal dye compound. H_3PO_4 reacting with the gel forms an insoluble metal phosphate and hence does not furnish the metal ions necessary to remove the dye.

2. The Preparation of Alizarine from Phthalic Anhydride and O-Dichlorbenzene. Max Phillips. Ortho dichlorbenzene and phthalic giving 3', 4'-dichlor-2-benzoyl-benzoic acid. This acid when heated with conc. sulphuric acid is converted into 2, 3-dichloranthraquinone. The 2, 3-dichloranthraquinone upon fusion with alkali is converted into alizarine.

3. Studies of Vapor Pressures of the Toluidines. J. F. T. Berliner and O. E. May. The vapor pressures of the three isomeric toluidines have been investigated

and methods are discussed for the preparation of toluidines of high purity. The vapor pressure equations and the equations for the heats of vaporization have been derived and the entropies of vaporization calculated.

4. Studies in Vapor Pressures of the Naphthols. O. E. May, J. F. T. Berliner and D. F. J. Lynch. The alpha and beta naphthols have been highly purified and their vapor pressures determined from temperatures at which they develop a pressure of about 1 mm. of mercury to temperatures somewhat about their normal boiling point. The vapor pressure equations and the equations for the latent heats of vaporization have been derived.

5. Studies in Vapor Pressures of the Mono-Nitro-Toluenes. J. F. T. Berliner and O. E. May. The vapor pressures of the three nitro-toluenes have been determined from a pressure of about 1 mm. to about 850 mm. of mercury. From these measurements the heats of vaporization and vapor pressure equations have been derived and the coefficient of association calculated. Methods for purification of the mononitrotoluenes are presented in this paper.

6. Why the Blue-Blooded Indanthrene Blue and GCD Show a Red Streak on Boiling. V. R. Kokatnur. It is well known that Indanthrene dyed fabrics become redder and brighter on prolonged boiling with water, soap or steaming. No dye books or the literature seem to give any reason for such a phenomenon. Production of redder or greener tones at will being commercially desirable, an underlying theory regarding the cause of such a change would be valuable. It is shown that the explanation lies in the oxidation of the hydrazine hydrogen gives greener tones.

VARIETY OF FABRICS MADE AT CAROLINA SCHOOL

A number of attractive samples of different fabrics made by students of the Textile School of the North Carolina State College are being distributed to the trade as examples of the range of work covered by the designing, manufacturing and dyeing courses of the school. The samples include narrow and wide sheetings, terry towel fabrics, shirtings, leno and Jacquard goods.

Nine companies belonging to the chemical section of the National Safety Council show average decreases of 29 per cent in accident frequency and 27 per cent in severity during 1923-1924, thus indicating canclusively that accidents can be prevented.

Senator Jesse H.. Metcalf, of Rhode Island, has recently endowed a plan by which the Providence branch of the National Safety Council is enabled to award a trophy named after the donor to the industrial plant in that city having the best accident prevention record for the year.

Current Fusions Within the German Dye Industry

By Trade Commissioner William T. Daugherty, Berlin

IN the course of its all-embracing expansion after formal fusion, approved by stockholders November 28, 1925, I. G. Farbenindustrie A. G. Frankfort-on-the Main, agreed on July 9, to a merger with Koeln-Rottweil A. G. (Berlin), Germany's largest war-time powder plant that has reordered its manufacture since the armistice to peace production from cellulose, of artificial silk, pyroxylin lacquers, film, cellophane, etc.

The "Agfa" and Bayer companies, of the Dye Trust, are making viscose and copper ammonia artificial silk, respectively; while, resulting from a recent community with the Vereinigte Glanzstoff Fabrik, of Elberfeld, the I. G. is taking up the manufacture of acetate silk, and is building a plant for this purpose at Perlin-Lichterfelde (Aceta G.m.b.H.). With I. P. Bemberg, of Barmen, it is erecting a copper ammonia plant at Dormhagen near Cologne. Its artificial silk interests are bound with Courtaulds of London and an American producer, so that the combination controls from 65 to 70 per cent of the world's production of artificial silk.

Production of Nitrocellulose Lacquers

In view of its dominant position, acquired a year or so ago, in the production of synthetic butanol and other solvents, the I. G. (Hoechster Farbwerke) is inaugurating production of nitrocellulose lacquers with the prospect of taking a leading position in this branch that has been indifferently exploited so far by some 100 small German producers with little effect against American competition. The "Agfa" is very conspicuous as a manufacturer of photo chemicals, film, etc. Kalle & Co., Biebrich/Rhein also of the I. G., makes cellophane. All of these interests will be extended by the pooling into I. G. operations of Koeln-Rottweil production.

Exchange of Shares Involved

The merger of the I. G. and Koeln-Rottweil will involve an exchange of the former's for the latter's shares in the ratio of 1 to 2. It was agreed that certain cartel companies belonging to Koeln-Rottweil will remain self-contained, but in mutual community of interests as herebefore, with assurance of the same dividends as paid under Koeln-Rottweil leadership. The latter passed dividends on 1925 business, but declared 6 per cent in 1924. The I. G. pays 10 per cent on 1925 operations, against 8 per cent in 1924. Cartel companies associated with Koeln-Rottweil include Dynamit A. G. vorn, Alfred Nobel & Co., Hamburg; Rhenish-Westfaelische Sprengstoffwerke A. G. Cologne; A. G. Siegener Dynamit

Fabrik, Cologne, and Deutsche Celluloid Fabrik A. G., in Eilenburg.

Possible Fusion with Dynamit Nobel

At the last general meeting of Dynamit A. G. vorm. Alfred Nobel & Co., it was disclosed that its current community of interest with Koeln-Rottweil might be succeeded by a fusion. In case of the latter, it would develop that Dynamit Nobel shareholders would trade their paper with the I. G. also in the above-mentioned ratio of 2 to 1. The Koeln-Rottweil-I. G. fusion was welcomed by Dynamit Nobel, inasmuch as the cartel relationship of the latter with Koeln-Rottweil has not been very satisfactory of late. A fusion of Dynamit Nobel with the I. G. would be favored, furthermore, by the circumstance that Nobel already secures about 80 per cent of its raw materials—notably for artificial silk manufacture—from the I. G.

Pooling of Technical Processes

The Koeln-Rottweil-Dynamit Nobel community of interest entered into an agreement last year with the British Dynamite Trust Company and an American firm whereby technical processes were pooled. This revived a pre-war working agreement. The two foreign companies bought in 15,000,000 marks of shares when Koeln-Rottweil and Dynamit Nobel each increased their capital by 7,500,000 marks. Before agreeing to fuse with the Dye Trust, Koeln-Rottweil is said to have gotten approval from its British and American associates.

Before and during the war, the Koeln-Rottweil Company was the largest powder plant in Germany. It furnished the army and navy with about two-thirds of its demand. In accordance with peace treaty provisions, it was compelled to reorder its production to a peace-time basis. This type of production, as noted above, duplicates part of the German Dye Trust's output, the latter having also been an extremely important factor in covering demand of the army and navy for chemical gases and high-powered explosives during the war.

The I. G's. Program of Expansion

I. G. Farbenindustrie A. G. Frankfort-on-the-Main, is following an intensive program of expansion and economy operation, in accordance with its announced purpose when it fused the six leading members of the Dye Trust last year and absorbed their subsidiary companies.

One conspicuous acquisition preceding that of Koeln-Rottweil was that of Stinnes shares of the Hugo Stinnes-Riebeck Montan & Oelwerke A. G., Halle/Saale in August, 1925. The Stinnes portfolio of shares amounted to 20,000,000 marks out of a total capitalization of 50,000,000 marks. The enterprise is based on lignite mining and distillation for a yield of mineral oils, montan wax, paraffin, candles, etc.

Since this acquisition, the I. G. has founded, in its stead, the Deutsche Gasolin A. G., of Berlin, for the initial purpose of marketing its new motor fuel, called "Motalin," introduced here in January, 1926. "Motalin" is a gasoline charged with "motyl" or iron carbonyl, calculated to provide an "antiknock" for internal-combustion engines. An American oil company and the Royal Dutch have each acquired 25 per cent of this company's shares.

Another comparatively recent acquisition was that, in 1924, of Rheinstahl, of Duisburg-Meiderich, a coal and coking enterprise with coal reserves especially suited to a yield of crudes for the I. G.'s dyestuffs. Previously, the I. G. owned since 1907 the Auguste Victoria pits in the Ruhr, but this one source of supply was insufficient to meet its needs. While acquiring initially 25 per cent of Rheinsthal shares, it is supposed that the I. G. has acquired more since, with a possible present majority interest in this enterprise.

Lignite—Fertilizers—Synthetic Fuels and Solvents

The expanding interests of the Dye Trust, particularly in the last couple of years, include, in addition to artificial silk mentioned above, lignite, synthetic fertilizers, light metal alloys, synthetic fuels and solvents.

The production of calcium, sodium, and barium for alloy by Griesheim, as well as cerium compounds to replace matches controlled here by a foreign trust, is noteworthy.

The carbide operations of this concern, however, for calcium cyanamide, but more significantly for a yield of synthetic acetic acid (in four plants), synthetic ethyl alcohol (in one I. G. plant) synthetic methanol at the Leunawerks, and synthetic butanol have assumed world-wide significance.

Further evidence of expanding interests is to be found, through its vertical application, in nitrocellulose lacquers by the Hoechster Farbwerks; lithopone, by acquisition recently of interest in the Schalke concern, of Gelsenkirchen, whereby the I. G. Bayer plant assumes a leading influence in the newly organized (April 1, 1926) Lithopone Syndicate, Cologne; industrial gases by Griesheim-Elektron in community with the "Gesellschaft fuer Lindes Eismaschinen;" and other synthetics.

Commanding Position Occupied by the I. G.

The German Dye Trust is misnamed, considering its current production. Its manufacture of dyes, though still important, is somewhat more than one-half its pre-war amount of production, but this one phase of manufacture is dwarfed, comparatively, when one takes into account the length and breadth of other lines of production cal-

culated to compensate for Germany's dye markets lost since the war in the face of foreign competition grown in the war interim.

The importance here of the I. G. to-day is so great that it occuppies a towering position. In viewing the German chemical industry, it must necessarily be looked upon as divided. One part—the major part—is the I. G. and its associated enterprises. The other is that division outside the I. G. (The Potash Trust might be excepted.) The I. G. has a capitalization exceeding that of all other German chemical enterprises combined. It declared a 10 per cent dividend in its last annual statement, whereas it is rather the exception than the rule that stockholders other than those of I. G. shares are so fortunate.

[Information concerning the financial status of German chemical companies may be obtained by properly qualified firms or individuals by addressing the Chemical Division, Bureau of Foreign and Domestic Commerce, Washington, D. C.]

RECENT PATENTS

Method of Preparing Artificial Silk Yarn for Textile Purposes

(1,590,784; June 29, 1926)

Suekichi Toda, of Sakai-Gun, Japan.

This invention relates to a method of preparing a yarn of artificial silk in unthrown or untwisted condition, characterized by the fact that a number of filaments come out of coagulating bath being passed through a solution of size and formed into a bundle of filaments or yarn, similar to a silk filament which consists of a number of raw silk fibers in unthrown condition closely adherent to each other by natural cericine. This invention has for its object to obtain artificial silk yarn which can be conveniently treated in textile working and can be glossed after it is woven or knitted.

To describe the process, viscose is first prepared and after pressing it out of capillary tubes into a coagulating solution filaments of artificial silk are obtained. The next step is to wash the filaments thus prepared in water, and to pass them, without having them thrown or twisted but in a bundle, through a solution of sizes such as gloiopeltis, gelatin, dextrine or other suitable materials with or without some softening agents such as wax, fat or resin according to the requirements. The solution of size, for example, is made by boiling together, for a sufficient time, 1.6 ounces of gloiopeltis and dextrine respectively, 0.25 ounces of gelatin and 0.8 ounces of wax in one gallon of water. When the filaments are taken out of the solution of size, they are closely adherent together into a yarn, which is then reeled or wound on bobbins.

The yarns thus produced meet the requirement of some kinds of weaving and knitting, of which the weft or warp or both in unthrown state is required or preferred. They have the advantage of improving the efficiency in textile working on account of their being coated with size so that the handling is facilitated. They are very like natural silk filaments in the following respects, that is, the coating material or size above described protects them from fluffs being produced in course of handling in the same way as the natural silk filament is protected by cericine, and secondly the coating material as well as stains made during the weaving or knitting step can be removed by desulphurating and bleaching after they are woven or knitted, just in the same way as cericine is removed by the process of glossing from the fabrics made of natural silk filaments so that luster is developed. The artificial yarn hitherto known has been thrown or twisted in order to retain the strength and firmness as the natural thrown silk yarn has, so that it gives a rough and hard sensation to the touch and has the disadvantage of their becoming attenuated and soiled in the course of treating. These drawbacks due to throwing can be successfully obviated by this invention.

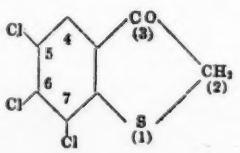
Violet Vat Dyestuffs of the 2-Thio-Naphthene-2-Indolindigo Series

(1,590,685; June 29, 1926)

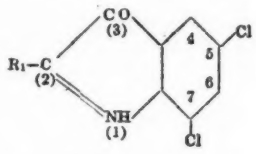
Richard Herz and Walter Brunner, Frankford-on-the-Main, Germany, assignors to Grasselli Dyestuff Corporation, New York, N. Y.

As a new compound a violet vat dyestuff of the 2-thionaphthene-2-indolindigo series corresponding probably to the formula:

which is when dry a violet powder, soluble in cold concentrated sulfuric acid to a bluish black, in warm concentrated sulfuric acid to a bluish green solution, which is separated therefrom in violet flakes, yielding with alkaline hydrosulfite an orange vat, from which cotton and wool is dyed in brilliant bluish, violet shades of an excellent fastness, especially to light, which dyestuff is substantially identical with the dyestuff obtainable from



by condensing it with an α-isatin body of the formula:



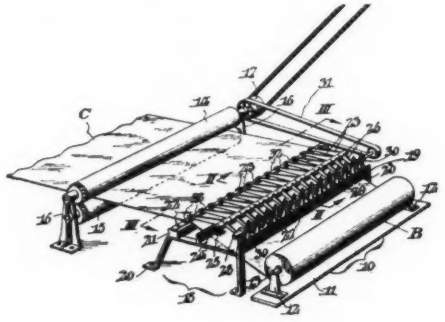
wherein R_1 means a halogen or an arylido group.

Cloth-Finishing Apparatus

(1,591,851; July 6, 1926)

John MacAdams and William Berry, Wilmington, Del., assignors to Joseph Bancroft & Sons Company, Rockford, Wilmington, Del., a Corporation of Delaware.

A cloth finishing apparatus comprising an aligned series of tappet hammers adapted to operate upon



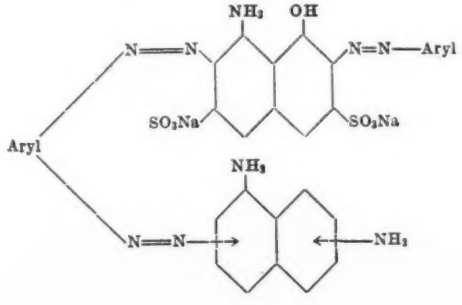
the cloth surface, the engaging faces of said hammers being cross-grooved and overlapping each other's provinces, and means to actuate said hammers.

Trisazo Dyestuffs and Process of Making Same.

(1,590,042; June 22, 1926)

August Leopold Laska and Fritz Weber, Offenbach-on-the-Main, Germany, assignors to Corporation of Chemische Fabrik Griesheim-Elektron, Frankfort-on-the-Main, Germany.

As new compounds trisazo dyestuffs having probably the general formula:



which are, when dry, bluish black bodies, soluble in water to a deep dark solution, yielding upon reduction with stannous chloride an arylamin, the 1-hydroxy-2.7.8-triaminonaphthalene-3.6-disulfonic acid, a para diamin base and a triaminonaphthalene, dyeing cotton and wool in bluish black shades and therefore especially adapted for dyeing mixed fabrics of cotton and wool.

Dyestuffs Containing Metals and Process of Making Same

(1,590,482; June 29, 1926)

Fritz Straub, Basel, and Herman Schneider, Riehen, near Basel, Switzerland, assignors to Society of Chemical Industry in Basle, Basel, Switzerland.

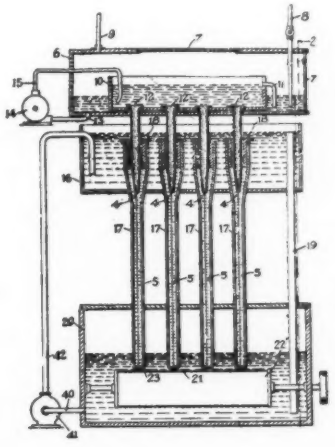
The herein described process for the manufacture of new dyestuffs by combining the substitution products of the 1-hydroxy-naphthalene-8-sulfamide with o-hydroxy-diazo-compounds not carrying any carboxyl group and containing not more than one nitro group and treating the dyestuffs thus obtained with agents yielding metals.

Treating Silk and Cellulose Material

(1,590,600; June 29, 1926)

Edwin Taylor, Brooklyn, N. Y., assignor to Taylor Laboratories, Inc., New York, N. Y.

The method of separating silk and cotton elements from silk and cotton mixtures, which consists in treat-



ing the mixture with a solvent of one of said elements to dissolve the same, said solvent not being a solvent of the other of said elements, separating the dissolved element from the undissolved element, and removing the solvent constituents from the dissolved element by electrolysis.

Technical Notes from Foreign Sources

Scientific Foundations of the Viscose Process

The chemical mechanism of the process of ripening of viscose as originally established by Cross and Bevan is upheld, and the data on which recent investigators have based a purely colloidal explanation are shown to be unreliable owing to imperfect purification of the xanthates examined. Viscose is the sodium dithiocarbonic ester of cellulose or alkali cellulose. Preparations, precipitated by alcohol, contain variable amounts of sodium hydroxide depending on the conditions of dilution. Xanthates precipitated and purified with sodium chloride are free from sodium hydroxide.

Ripening is simply a process of hydrolysis of the ester with elimination of sodium hydroxide and carbon disulphide, these products then undergoing secondary reactions, principally with formation of sodium trithiocarbonate. The primary product of complete xanthogenation is the C_{12} xanthate in the ratio $(C_6H_{10}O_5)_2$:CS_2; NaOH. No evidence could be obtained of the formation of a C_6 xanthate nor of any higher degree of xanthogenation. When the proportion of carbon disulphide is restricted to the amount theoretically necessary to produce the C_{12} xanthate (23.6 per cent of the cellulose), there is difficulty in preparing a homogeneous solution and the stability of the viscose does not become normal until the C_{24} stage has been reached.

A properly soluble viscose is not obtained unless the concentration of the mercerizing sodium hydroxide has been sufficient to produce the alkali cellulose compound $(C_6H_{10}O_5)_2$.NaOH. In practice a slightly higher concentration is desirable. The same law holds in the case of the hydroxides of the other alkali metals, lithium, potassium and rubidium, all of which gives "viscoses" if employed at equivalent concentrations.

The solvent powers of normal solutions of the hydroxides of the alkali metals decrease as the atomic weights increase. For comparative purposes the products of xanthogenation may conveniently be dissolved in normal sodium hydroxide. For instance, a rubidium xanthate gave an imperfect viscose when dissolved in sodium hydroxide. The latter viscose, however, yielded a pure rubidium xanthate when neutralized and precipitated with salt. Viscose solutions are most stable against coagulation when they contain 8 per cent of free sodium hydroxide. This also corresponds with the condition of minimum viscosity.

The effects of by-products (salts) and of higher concentrations of sodium hydroxide is to hasten coagulation. The complexity of the cellulose molecule or its degree of dispersion, as measured by the viscosity of the regenerated product in cuprammonium, undergoes a quick change after the immersion in the mercerizing liquid, the viscosity falling in six hours from 75 to 25. During the aging of the alkali cellulose the fall in viscosity proceeds more slowly to 12.3 after three days. During the xanthate reaction another quick drop in viscosity to 8.3 is recorded, after which, during the ripening of the viscose, very little change in the cellulose complex can be detected.

The changes in the viscosity of the viscose itself are initially influenced by colloidal physical conditions. The dispersion of the cellulose xanthate requires an appreciable time or vigorous mechanical treatment. The viscosity of freshly prepared viscose is fairly high and falls, as dispersion becomes more complete, to a minimum after 24 to 48 hours. Subsequently there is a steady rise in viscosity during ripening, attributable to loss of ester groups from the xanthate and accumulation of saline by-products in the solvent. The rise in viscosity immediately before coagulation is very rapid. (Cellulose Chemie, volume 7, pages 17 to 55.)

Soluble Products from Vat Dyes

Vat dyes in solution or suspension in a suitable organic base, are treated with an alkylsulphuric acid halide in the presence of a metal. The leuco-derivatives thus obtained are, in general, soluble in hot water and alkalies and sometimes also in acids, and may be used for dyeing animal or vegetable fibers or artificial silk.

The parent dye may be regenerated on the fiber by treatment with a mild acid oxidizing agent, such as acid ferric chloride. The dye may or may not be refluxed with the base and metal and cooled before the addition of the alkyl sulphuric acid halide. An acid or an acid salt may be added to the mixture of dye, metal and base. The process is applicable to indigoid dyestuffs, such as Indigo and dichlorodibromoindigo, and to anthraquinone dyes, such as, benzanthrone, indanthrone, flavanthrene, pyranthrone and anthraquinone-acridone dyes.

The metal is usually zinc dust, but iron, cobalt, copper, aluminum, cadmium, tin, copper bronze, and a mixture of zinc and iron may be used. Methyl sulphuric acid chloride is usually employed, but ethylsulphuric acid chloride is also suitable. Tertiary organic bases are used, usually pyridine dimethylaniline, quinaldine and quinoline may be employed and diluents, such as chlorobenzene or carbon disulphide, may be added. Suitable acidic substances are hydrochloric and acetic acids, zinc and stannous chlorides, sodium bisulphite and pyridine hydrochloride.

In general cold water is added to the reaction mixture and the product is obtained as an undissolved powder..

The nature of the primary products is unkown, but there is no evidence that they are alklyl sulphuric esters. That from Indigo is a methylpyridinium derivative of indigo-sulphuric acid. Condensation is usually effected at the ordinary temperature, but with flavanthrone a temperature of about 80 deg. Cent., is used and the metal is copper or copper bronze powder. (British Patent No. 247,787.)

Dyeing and Printing Textile Materials

The fastness to washing of dyeings with direct cotton colors is improved by dyeing with water-soluble zinc or magnesium compounds of the coloring matters in the presence of ammonium salts together with ammonia or soduim bicarbonate in quantity insufficient to precipitate basic compounds. Zinc or magnesium compounds of the dyestuffs are deposited in the fibers, where they are subsequently fixed by heating or steaming. Ammonia or sodium bicarbonate need not be added if ammonium salts of volatile acids, such as ammonium acetate, are used.

For example, 100 pounds of cloth are dyed in a 200-gallon bath which contains 3 pounds of the dyestuff, 75 pounds of magnesium sulphate, 18 pounds of ammonium sulphate, and 5 gallons of ammonia (density 0.88), the ammonia being added fifteen minutes after the other constituents of the bath. Compositions which contain the water-soluble zinc or magnesium compounds may be used for printing. (British Patent No. 247,694.)

Exposure Tests with the Osram Pointolite Lamp

An arc lamp filled with an inert gas and containing two hemispherical tungsten electrodes which are separated with formation of an arc (when the electric current is first passed through the lamp) by the expansive force produced by the heating of a bimetallic strip, gives light, particularly when the red rays are reduced by passage through a screen of water, which is especially suitable for carrying out fading tests and the comparison of color tones. The light obtained from the lamp is uniform over considerable periods and is suitable for carrying out quantitative measurements. (Textilberichte, volume 6, 914-6.)

New Process of Dyeing Wool with Alizarine Black WX Extra

An investigation was undertaken to develop a simple and expeditious process for dyeing with Alizarine Black this being interesting for a number of reasons, namely, the demand for solid black dyed fabrics, the sensitiveness and prolonged character of the dyeing process at the present time and the fact that Alizarine Black is the only black that is absolutely fast.

The difficulty in dyeing Alizarine Black on bobbins of combed wool, either in the ordinary vat or in a dyeing machine, rests in the fact that aphthazarine is possessed of only a slight degree of fastness, the dyeings becoming very irregular, bronzing almost always and not being fast to rubbing.

It appears logical that in starting with naphthazarine bisulphite, it should be possible to obtain better results, this color being perfectly soluble. Nevertheless, naphthazarine bisulphite does not dye wool in the neutral bath. The addition of acetic acid serves only to fix a part of the dye and this is accomplished only with forced boiling, which is injurious to the fibers. Sulphuric acid, on the other hand, decomposes the bisulphite too quickly. It is therefore necessary to employ an acid which does not possess these inconveniences. Formic acid, whose acidic properties place it between acetic and sulphuric acids, was indicated in this case.

This acid, in fact, allows gradual and complete fixation of the color conditions which are the *sine qua non* of good dyeing. It was found useless to start with the bisulphited Alizarine Black in practical work. The bisulphite can better be formed right in the color liquor. The dyeing is carried out in the following manner.

The dye bath is raised to a temperature of 50 to 60 deg. Cent. Then a 440 deg Be. solution of sodium bisulphite is added in the proportion by weight of one-half to three-quarters of the weight of the dye. The wool is wet down in this bath for a period of fifteen minutes. In using apparatus which are provided with reservoirs, the dye liquor is allowed to flow into the reservoirs, and in using apparatus without any special containers for the liquor, the bobbins themselves are removed. The color is added through a fine screen and the mixture is then agitated for several minutes. The dye dissolves and the color of the solution becomes brownish yellow. The bobbins or spools are then replaced or the liquor is allowed to flow back into the bath from the reservoirs. The temperature of the liquor is maintained at 60 deg. Cent., for fifteen minutes, and then 1 per cent of formic acid is slowly added and the liquor raised to the boiling point within a period of fifteen minutes. The circulation of the liquor is reversed and another 1 per cent of formic acid is added. The liquor is exhausted within a period of thirty minutes. The wool is then chromed in a fresh liquor containing 1½ to 2 per cent of sodium chromate, the liquor being employed at the boiling temperature.

The quantity of formic acid that must be added to exhaust the bath bears a direct relation to the quantity of sodium bisulphite employed. The more bisulphite must be added to dissolve the dyestuff, the more formic acid must be added to exhaust the bath. In the case of Brilliant Alizarine Black the minimum proportion of sodium bisulphite is ½ per cent of the weight of the dye. This means the use of 2 per cent of formic acid, 85 per cent concentration.

The blacks obtained in this manner are fast to all tests. The dyeing of Alizarine Black WX extra is the same in all details as that of Brilliant Alizarine Black. (Revue Generale Matieres Colorantes, 1926, page 374.)

JAPANESE INDIGO PRODUCTION

The 1925 production of natural Indigo paste on the Island of Taiwan (Formosa) amounted to 3,067,379 pounds, a small increase over the 1924 total of 3,043,500. The production is for the most part consumed locally as Indigo-dyed cloth and is a staple requirement of the large Formosan-Chinese population. Of the 1925 production, the total exports amounted to only 35,992 pounds, valued at $1,380, and were consigned to China. The area devoted to the growing of Indigo, approximately 3,900 acres, has not varied materially in the past twenty years, although since the Japanese occupation tea cultivation has eliminated Indigo in some sections.

It is stated that synthetic Indigo is being produced by the Mitsui Mining Company. The quality and price of this domestic product is said to campare very favorably with the German dye. The receipts of synthetic Indigo from Germany, the source of over 90 per cent of such imports, declined during 1925 to 2,100,000 pounds from a total of over 3,000,000 in 1924.

NEW INDANTHRENE DYESTUFFS OF I. G.

Four new indanthrene dyestuffs were recently developed by the Hoechst plant of the I. G. Farbenindustrie and placed on the German market, according to Consul Claiborne, Frankfort-on-Main.

(a) Indanthrene printing Brown 3R paste, intended for printing according to the potash steaming process. The prints are non-fading and genuine.

(b) Indanthrene printing Violet BBF paste and RF paste, also applicable for printing, and perfectly genuine.

(c) Indanthrene Blue 8 GK. (No comments rendered as to application.)

(d) Indanthrene Golden Yellow GK double paste, especially manufactured for dyeing and printing vegetable fiber materials, and has proven unfadable and genuine.

According to information from reliable sources, these dyes have already been exported to various countries.

SOUTHERN TEXTILE EXPOSITION PLANS COMPLETED

W. G. Sirrine, President of the Southern Textile Exposition, announced last week that all the plans for the next Exposition, November 1 to 6, in Textile Hall, Greenville, S. C., are completed.

The land adjoining Textile Hall has been secured for the huge steel annex which will be placed thereon. It will be two hundred feet long and sixty feet wide, and will house some of the most important exhibits.

Every committee has been appointed and is at work. The program for the week is being laid out by the Citizens' Committee, of which Capt. Reid Elkins is chairman, and all the other committees are closely co-operating with them. There will be something going on every day during the Exposition, the principal event being the Convention of the Southern Textile Association. The arrangements for the entertainment of this body is in the hands of the Convention Committee, of which Edwin Howard is chairman.

It will give general satisfaction to all the exhibitors to know that Earle Mauldin, who is now a resident of Florida, has consented to return to Greenville and be associated with the Exposition as manager. Mr. Mauldin thoroughly understands the work of exposition management and is personally acquainted with practically every exhibitor. He is an experienced engineers and contractor and will have charge of the erection of the steel annex and the putting of the equipment therein.

INCREASE IN SOUTH AFRICAN IMPORTS OF COAL TAR DYES

The importation of coal-tar dyes into the Union of South Africa increased from 3,390 pounds, valued at £731 in 1924 to 18,659 pounds, valued at £2,998 in 1925. Germany and England shared the bulk of this trade. Holland and Switzerland participated to a small extent but the United States was not listed as a source of these imports.

There is no production of coal-tar dyes within the Union. Two woolen mills and a growing number of shoe factories and tanneries constitute the dye-consuming industries. Although household dyes, imported largely from Great Britain, enjoy a brisk demand, the increased importation of colors is probably due to the expansion of the shoe and leather industries and the subsequent increased demand for leather dyes.

THE SWISS DYE TRADE

The Swiss dye industry has suffered during the past quarter from the slackness in the British textile industry; England dropped from first to third position as an importer of Swiss dyes.

Exports of aniline dyes to the United States during the second quarter of 1926 showed a slight reduction in value but there was actually an increase in quantity. The value of the exports amounted to $345,798, as compared with a value of $418,325 in the first three months of the year. In 1925 the shipments to the United States during the corresponding quarter (the second) amounted to 320,798 pounds, valued at $352,700. (Consul Calvin M. Kitch, Basle, Siwtzerland.)

The advertised foreclosure sale of the Cochrane Print Works, Malden, Mass., was postponed at the last minute on August 20, by order of the Superior Court.

NEW DU PONT DIAZO COLOR

Pontamine Diazo Green 2 GL, a new developed color, has recently been placed on the market by the Dyestuffs Department of E. I. du Pont de Nemours & Co. The manufacturers consider this an important addition to their diazo lines, as heretofore they had no green in this group. When diazotized and developed, this new color produces greens said to be of exceptional fastness, especially to water, acid and washing. The use of Pontamine Developer Z is recommended with this color, but beta-napthol can be used so that the new green can be combined with any of the diazo colors. Pontamine Diazo Green 2 GL is described as easily soluble and level dyeing. It is stated in the announcement that it is particularly useful for pure silk being dyed either from a neutral or an acid bath, and that the fastness on silk is in every way equal to the fastness on cotton. On rayon deep shades are obtained. Celanese effects are left practically unstained. Pontamine Diazo Green 2 GL yields fairly good unions on cotton-silk materials and can be recommended for this purpose whenever fastness is desired. This color discharges to a clear white on cotton and silk so that it may be used for a ground color for such work.

NEWPORT ISSUES RED VIOLET PASTE

A leaflet distributed by the Newport Chemical Works, Inc., of Passaic, N. J., describes the properties of a new dyestuff for cotton and rayon, put on the market under the name of Antherene Red Violet RRN Paste. This color is said to possess excellent qualities for dyeing cotton, rayon and silk in all forms, and to be exceptionally level dyeing and consequently of interest as a shading color. Its general excellent fastness, says the announcement, makes it valuable for the production of shades on dress goods, shirtings, ginghams, bedspreads, etc.

The leaflet shows dyeings of this new violet on rayon and cotton swatches and gives in detail the fastness properties and method of application.

THREE NEW NATIONAL DIRECT DYES

Among the most recent additions to the line of fast-to-light direct colors manufactured by the National Aniline & Chemical Company, Inc., are National Solantine Pink 4 BL and Solantine Blue 2 GL. Another direct color just put on the market by this manufacturer is National Erie Black RF, as a companion product to Erie Black BF.

The Solantine Pink 4BL produces shades much bluer than Solantine Red 8BLN and is particularly useful where delicate tones are desired. According to the description of this color it possesses excellent solubility and level dyeing properties and is recommended for application to cotton and rayon and for union dyeing, in which animal fibers are practically unstained. Excellent whites are said to be obtained when the color is discharged with hydrosulphite. The paper trade should find it useful for the tinting of bonds where special light fastness is required.

National Solantine Blue 2GL, it is claimed, also possesses excellent solubility and good level dyeing properties and is resistant to the influence of metals, thereby making it well suited for use in all types of dyeing machines. It is most useful for the dyeing of cotton and rayon and for union styles in which animal fibers are left practically clear. Its dischargeability with hydrosulphite recommends it to the printing trade, while its fastness to light and resistance to acid and alkaline adhesives is said to make it desirable for paper.

Erie Black RF is described as possessing properties very similar to those of National Erie Black BF, being of good solubility, dyeing level and staining acetate silk but slightly. It is recommended for the dyeing of cotton, rayon, pure and tin weighted silk and cotton and silk hosiery. It will also be found useful as a speck dye and in the dyeing of leather and paper.

TETRAMINE FAST GREY S

After considerable research the United Chemical Products Corporation has developed a Tetramine Fast Grey S, a self-color described as having properties that make its fastness to light and washing very good. The fastness to light of this color is the same as this manufacturer's Direct Fast Black L, and is redder in shade. According to the announcement, Tetramine Fast Grey fills a gap in the range of fast direct colors.

INDEPENDENT SILK DYEING COMPANY ENLARGES PLANT

A number of new installations of equipment, new additions to several departments, consolidation of others and various minor changes have been made in the plant of the Independent Silk Dyeing Company, Inc., of Farmingdale, L. I.

The capital stock was recently increased from $100,000 to $200,000. A new addition has been built for the finishing department, a modern brick and steel sash construction, all north light, giving 20,000 square feet of floor space. The skein dyeing department has been consolidated, making 10,000 square feet, one building unit, available for piece dyeing. The firm has installed the latest types of machinery for piece weighting, and will specialize in weighted crepes and georgettes, and the better grades of pure dyed crepe and georgette, as well. To facilitate business an additional boiler of 250 h. p., with all ac-

cessories, and a hot water supply system of 40,000 gallons per hour capacity, have been installed. The plant has a plentiful supply of water of less than one degree hardness, which will secure the same degree of success in the piece dyeing department that the company has attained in skein work. Robert Kampshulte, who has had years of experience in piece dyeing and finishing in Paterson plants, and who is well known in the trade, will have charge of the piece dyeing department. All of the new machinery installed being of the latest type, and the dye work being carried on by skilled workers, a minimum of mechanical and manual handling is assured.

HOLES IN WHITE HOSIERY TRACED TO ELECTROLYSIS

A problem, apparently of a chemical character, concerned with the forming of holes in ladies' white hosiery in the bleaching process, turned over to the Bureau of Standards for investigation, has been solved by the discovery that the holes were caused primarily by a mechanical discrepancy in the bleaching tank, not by acid reaction, it has been announced in a statement issued by the bureau.

The statement says that several samples of this white hosiery were submitted in which "holes had been made, presumably during the bleaching process." It was learned that this hosiery had ben bleached in a prepared bleaching solution, which was of acid reaction.

"A study of this problem showed that the hosiery had come in contact with exposed copper or iron nails in the bleaching tank, which created a metallic stain," the statement said. It was further explained that "the holes resulted from a 'tendering' of the hosiery in these places, caused by an electrolytic action set up by the metallic stain and the peroxide."

As a remedy for this shortcoming, the bureau recommended "that every care should be exerted that the nails be embedded below the surface of the wood so that they could not come in contact with the hosiery at any time. Periodic inspection of the tanks and wooden lattice linings might result in minimizing the losses from the condition."

This problem was undertaken, it was stated, in connection with the research associateship established at the bureau by the National Association of Hosiery and Underwear Manufacturers, in connection with which defects are submitted to the bureau through the association's office for study.

SILK WASHING METHODS WORKED OUT

The popularity of washable silks has produced some disconcerting results. Much alleged to be washable often loses weight, color and reputation in its passage through the tub and wringer. On the other hand, much that, from the care taken in its manufacture, actually should stand proper washing is ruined because the washer lacks knowledge of the correct methods. The problem was studied intensively by Cheney Brothers and a set of washing methods worked out which should be most helpful in improving laundry practice.

Extravagant and ill-judged claims are often made as to the amount of abuse that silk will stand in washing. Such claims are bound to lead to disappointment. It does not suffice to have colors which will withstand heat and poor soaps, if abusive treatment results in the deterioration or destruction of the fabric itself. Washing in extremely hot or boiling water, using rubbing boards and wringers, and pinning on to the clothes line, will give bad results.

If the following washing directions are observed, properly dyed wash silks will give long wear and preserve their full value:

1. Use a good grade of neutral soap producing thick suds with hot water; then add enough cold water to make it tepid (100 deg. Fahr.). (Leading soap manufacturers produce soaps which are suitable for washing silks, and the educational campaigns which they conduct are serving to spread reliable information on correct laundering methods for silk.)

2. Work the suds through the fabric for not more than five minutes time. Do not rub nor twist it but gently squeeze out the suds.

3. Rinse well in tepid water immediately after washing. Squeeze thoroughly but do not twist.

4. Roll in dry cloth and let stand until slightly damp, then press with a moderately hot iron.

5. Washable goods should not be dried in the sun. They should not be pressed with a too hot iron.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i. e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

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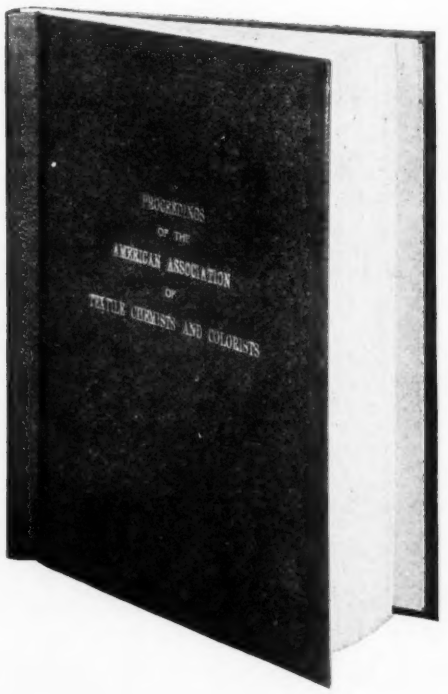

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